RESEARCH ON SPUTTERING OF FERROELECTRIC THIN FILMS

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The magnetron sputting technique has been used to grow ferroelectric thin films of tungsten bronze (T.B.) PBN:60 and SBN:75, and perovskite PLZT. Film crystallinity was found to be strongly influenced by substrate temperature, with temperatures of 500-600°C usually required. Polycrystalline films were grown on quartz, sapphire and glass substrates, whereas oriented crystalline films of PBN:60 and SBN:75 were achieved with SBN:60 substrates, which have a close lattice match. The PLZT films grown on SBN:60 substrates are grain-oriented along the [100]-orientation and have excellent surface texture. This is the first time such films have been grown on T.B. substrates.

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1.0 PROGRESS SUMMARY

This report covers work on sputtered ferroelectric thin films carried out over the period of May 1, 1987, to April 30, 1988, in the Ferroelectric Materials Department of the Rockwell International Science Center under Contract No. F49620-86-C-0052. The period covered by this report is the second year of this three-year program. During this period, significant progress has been made in the growth of thin films of tungsten bronze $Pb_{0.6}Ba_{0.4}Nb_2O_6$ (PBN:60), $Sr_{0.75}Ba_{0.25}Nb_2O_6$ (SBN:75), and perovskite PLZT.

The advantages of ferroelectric thin films for optoelectric applications have not been fully exploited in this country due to the difficulties of achieving single crystal films of adequate quality. Isolated examples of successful growth have been reported on such materials as $LiNbO_3$ and $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN:50) for optical wave guides and surface acoustic waves using liquid phase epitaxial (LPE) techniques. Based on work reported in literature, LPE growth is suitable for only lattice-matched substrate materials, and in some instances, film quality is a severe problem due to the inclusion of solvents. For this reason, the magnetron sputtering technique has been used extensively to explore simple, as well as complex, ferroelectrics based on Pb^{2+}-containing solid solutions.

Three imortant ferroelectric compositions (tungsten bronze PBN:60, SBN:75 and perovskite PLZT) have been selected in the present study. We selected PBN:60 because it appears close to the morphotropic phase boundary (MPB) and possesses an exceptionally large longitudinal electro-optic coefficient ($r_{51} = 2300 \times 10^{-12}$ mV) with very large polarization (≥ 70 μcoul/cm^2). SBN:75 is also a very important material since it exhibits an electro-optic coefficient in excess of 1400×10^{-12} m/V. The PLZT composition which is selected in the present study also exhibits a large electro-optic coefficient ($r_{51} > 1000 \times 10^{-12}$ m/V) with large polarization.

The growth of tungsten bronze thin films has been highly successful using bronze substrate material such as SBN:60. At present, the growth of PBN:60 and SBN:75 has been studied in three different orientations, e.g., (001), (100) and (110), with great success and this is the first time these films are available for device studies. Orthorhombic and tetragonal tungsten bronze forms are related to each other in the following way:

$(110)_{tetra} = (100)_{ortho}$

Although the growth of PBN:60 and SBN:75 has been successful on the (110)-oriented SBN:60 substrates, we believe that both the tetragonal and orthorhombic forms coexist in this orientation. However, at present, it is not known how to stabilize these forms independently with respect to this orientation. Further study is underway to determine structural stability with respect to temperature and other growth conditions.

We have also been successful in growing PLZT thin films in both polycrystalline and single crystal form using various substrates. For example, when glass, Si or quartz were used as substrates, the films were polycrystalline and showed the pyrochlore phase below 600°C. On the other hand, films grown on SBN:60 substrates were single crystal and we did not observe the pyrochlore phase at any growth temperature. This is a unique advantage for developing single crystal PLZT films, and we believe that this is the first time PLZT thin films have been produced on tungsten bronze substrates. The availability of these films should make a significant impact on various device applications such as spatial light modulators (SLM), guide wave optics, pyroelectric detectors and SAW.

PLZT thin films grown on Si substrates show great promise for SLM, although the films are polycrystalline. Although the resolution of the films is sufficient, we suspect that if single crystal films are employed for SLM studies, the overall performance should improve significantly. For this reason, we are currently attempting to evaluate single crystal films grown on both Si and SBN:60 substrates. We also believe that performance should also be enhanced with PBN:60 films.

In the third year, we plan to explore only PBN:60 and PLZT thin films for optical applications and will determine their usefulness for these applications. Besides these applications, we will also explore their use in SAW and pyroelectric detector applications.

As a result of the first and second year efforts, several technical effort papers summarizing our progress have been prepared and will be submitted for publication. This report includes drafts of these papers.

2.0 GROWTH OF TUNGSTEN BRONZE SBN:75 AND PBN:60 THIN FILMS

2.1 Introduction

The use of ferroelectric thin films for optoelectronic applications is being actively pursued by researchers in Japan as well as in the U.S.S.R.[1-8] The state-of-the-art for both the growth techniques and applications has been pushed largely by the Japanese. In particular, integrated optics concepts are being realized through the development of sputttered or epitaxial ferroelectric films. The novel concept of integration through the use of semiconducting substates, e.g., growth of $BaTiO_3$ on InSb and GaAs by Iida,[2] has recently emerged. The advantates of such integration include both reduced cost and enhanced device performance.

The growth of ferroelectric films, as opposed to thin samples prepared from bulk single crystals, offers numerous advantages as summarized in Fig. 1. First, the growth of ferroelectric single crystals of optical quality is complicated by growth problems arising from structural phase transitions, i.e., cycling from a high symmetry paraelectric to a low symmetry ferroelectric form, and secondly, from the complex phase diagrams. Even where successful growth of optical quality crystals (for example, $Sr_{1-x}Ba_xNb_2O_6$ (SBN), $Ba_{2-x}Sr_xK_{1-y}Na_yNb_5O_{15}$ (BSKNN)[9] and $LiNbO_3$) has been achieved, the preparation of properly oriented thin samples from crystals is extremely difficult due to the following problems:

1. Orientation of crystals within an accuracy of ±1°.
2. Parallelism of crystal faces.
3. Introduction of defects (e.g., cracks) by polishing.
4. Poling of crystals, particularly when the Curie temperature is over 250°C.

Although the figures-of-merit for optical applications are still excellent for such samples, performance is degraded by the loss of spatial resolution and optical quality. For these reasons, the optical community prefers as-grown films for optoelectronic device applications. The potential applications for ferroelectric films are summarized in Fig. 2 along with their figures-of-merit.

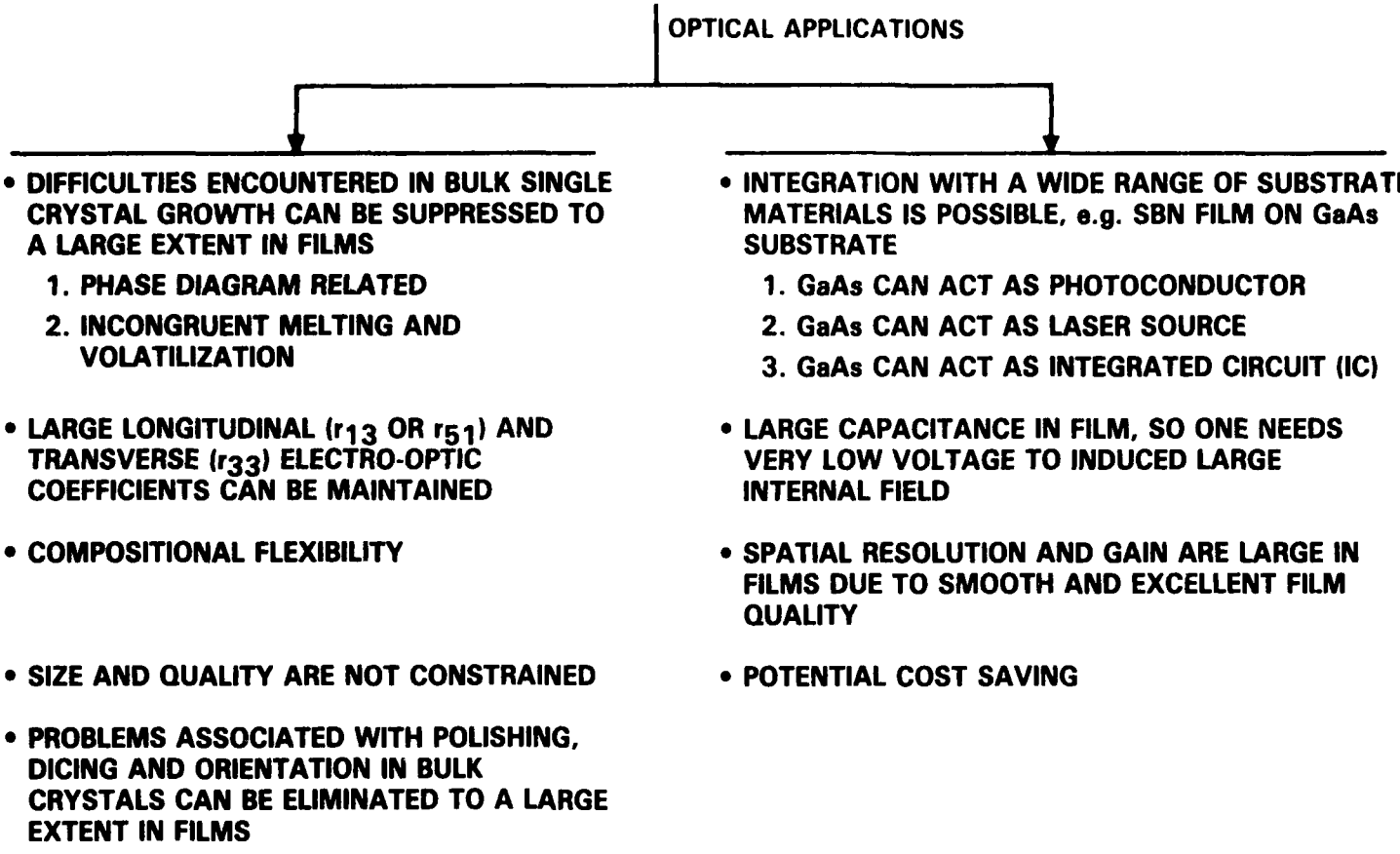

Fig. 1 Justification for the development of ferroelectric films.

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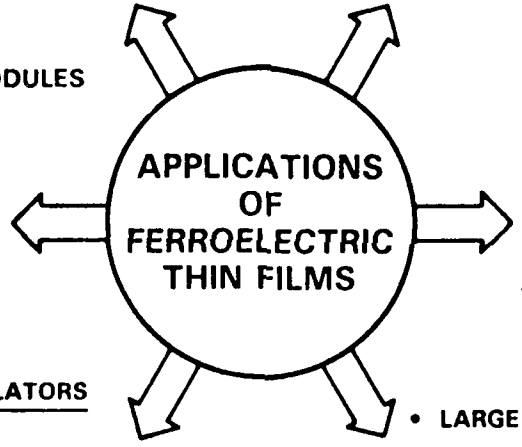

PIEZOELECTRIC AND ELECTRO-OPTICS

- LARGE k^2 AND d_{33}/ε
- TEMPERATURE COMPENSATED ORIENTATIONS
- GRAIN ORIENTED TO SINGLE CRYSTAL FILMS
- THICKNESS GREATER THAN 8 μm

SUBSTRATES: SBN, ZNO, GLASS, GaAs

APPLICATIONS: FILTERS, RESONATORS, SENSORS (UNDERWATER), ADAPTIVE OPTIC, PHASE MODULES

PHOTOREFRACTIVE

- LARGE $n^3 r_{ij}/\varepsilon$
- SINGLE CRYSTAL FILMS
- THICKNESS ~ 5 μm

SUBSTRATES: GaAs OR SBN

APPLICATIONS: ERASABLE STORAGE

SPATIAL LIGHT MODULATORS

- LARGE r_{51} OR r_{13}/ε
- SINGLE CRYSTAL FILMS
- THICKNESS 1 TO 5 μm

SUBSTRATES: GaAs, SI, SBN

APPLICATIONS: OPTICAL SIGNAL, PROCESSING, INCOHERENT-TO-COHERENT CONVERSION

NEW OPPORTUNITIES?

GUIDED WAVE OPTICS

- LARGE r_{ij}/ε
- LOW OPTICAL LOSSES
- THICKNESS 3-5 μm
- SINGLE CRYSTAL FILMS

SUBSTRATES: GaAs, SI, SBN

APPLICATIONS: WAVEGUIDES, SWITCHES, MODULATORS

PYROELECTRIC DETECTORS

- LARGE p/ε
- LOW TAN δ
- THICKNESS ~ 1 μm
- GRAIN ORIENTED TO SINGLE CRYSTAL FILMS

SUBSTRATES: NONFERROELECTRICS

APPLICATIONS: UNCOOLED FOCAL PLANE ARRAYS, VIDICON

Fig. 2 Device concepts for ferroelectric thin films.

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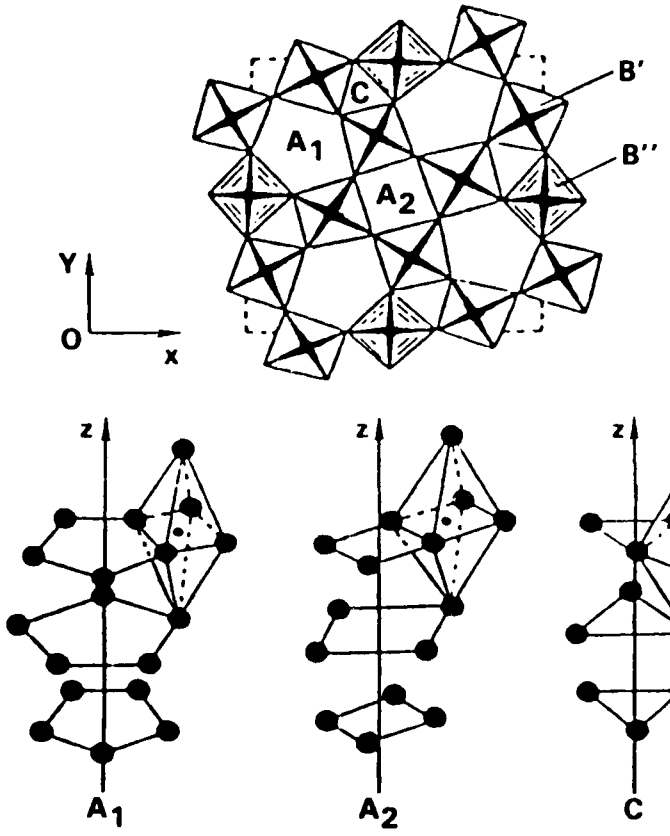
Based on these figures-of-merit, the current best ferroelectric materials are perovskite $BaTiO_3$ and tungsten bronze SBN:60, SBN:75 and BSKNN. However, many other ferroelectric compositions exist which exhibit much higher figures-of-merit (at least 5-10 times better). Unfortunately, these compositions can presently be prepared only in ceramic form or as millimeter-size crystals. Typical of these are tungsten bronze $Pb_{1-x}Ba_xNb_2O_6$, perovskite $PbZr_{1-x}Ti_xO_3$ (PZT), $Pb_{1-x}La_xZr_{1-y}Ti_yO_3$ (PLZT), and layered structure SbSI and $Bi_4Ti_3O_{12}$. Many of these compositions exhibit an MPB region where all optical and dielectric constants are exceptionally large. The primary growth problems associated with these materials are lead loss, the cracking of crystals due to inhomogeneity and the first order phase transition behavior in many of these compositions. These problems have prevented serious consideration of these materials for device studies.

In the present work, we examine the epitaxial thin film growth of the tungsten bronze compositions $Pb_{0.6}Ba_{0.4}Nb_2O_6$ (PBN:60) and $Sr_{0.75}Ba_{0.25}Nb_2O_6$ (SBN:75) using the sputtering technique. SBN:60 substrates appear to be suitable and the films produced on these substrates are of single crystal quality. This paper reviews the growth of tungsten bronze films using the sputtering technique and their applications.

2.2 Background on Current Ferroelectric Materials

Ferroelectric tungsten bronze oxides have been studied for their electro-optic and pyroelectric properties[10-13] and have been found to be effective for many related applications. The bronze compositions can be represented by the general formulae as $(A_1)_4(A_2)_2C_4B_{10}O_{30}$ and $(A_1)_4(A_2)_2B_{10}O_{30}$, in which A_1, A_2, C and B are 15-, 12-, 9- and 6-fold coordinated sites in the crystal lattice structure. The tetragonal bronze prototypic structure is shown in Fig. 3 in projection on the (001) plane.[13] A wide range of solid solutions can be obtained by substituting different A_1, A_2 and B cations, and a number of different types of ferroelectric and ferroelastic phases have been identified (over 100 compounds and solid solutions). The ferroelectric phases can be divided into two groups: those with tetragonal symmetry (4 mm), which are ferroelectric, and those with orthorhombic symmetry (2 mm), which are both ferroelectric and ferroelastic.



- **CHEMICAL FORMULAE**

  $(A_1)_4(A_2)_2C_4B_{10}O_{30}$ = FILLED STRUCTURE

  $(A_1)_4(A_2)_2B_{10}O_{30}$ = UNFILLED STRUCTURE

  A_1 = 15-FOLD COORDINATED SITE

  A_2 = 12-FOLD COORDINATED SITE

  C = 9-FOLD COORDINATED SITE

  B = 6-FOLD COORDINATED SITE (TWO SITES)

- **CRYSTAL STRUCTURE**

  4/mmm TO 4mm (TETRAGONAL-TETRADONAL)
  4m mm TO mm2 (TETRAGONAL-ORTHORHOMBIC)

- **KNOWN SYSTEMS**

  150 COMPOUNDS OR MORE
  SOLID SOLUTIONS BETWEEN END MEMBERS
  SEVERAL MORPHOTROPIC PHASE BOUNDARY SYSTEMS

- **PROPERTIES**

  LARGE ELECTRO-OPTIC, PYROELECTRIC AND PIEZOELECTRIC
  COEFFICIENTS – DEPEND ON PROTOTYPIC PHASE

Fig. 3 Projection of the tetragonal tungsten bronze crystal structure on the (001) plane.

Table 1 summarizes the current best tungsten bronze compositions for optical and nonlinear optical applications. Since the figures-of-merit for optical and photorefractive applications are taken as r_{ij}/ε, $n^3 r_{ij}$ and $n^3 r_{ij}/\varepsilon$, respectively, it is important that one examine bronzes exhibiting large electro-optic coefficients, and at the same time be relatively easy to grow in thin film form. Based on our work in this family, we have found the tetragonal bronze compositions to be promising, and several of these compositions have been grown in our laboratory as well as in Japan.[3-8] Of the total group of tetragonal bronzes, the SBN and PBN solid solution films have been selected in the present work. SBN solid solution crystals exhibit a strong transverse (r_{33}) electro-optic coefficient,[9,10] whereas strong longitudinal (r_{51}) and transverse (r_{33}) electro-optic coefficients have been observed for PBN crystals. The phase relation and crystal growth problems associated with each system are discussed below, together with the potential optical interest in each.

Table 1

Leading Electro-Optic Tungstent Bronze Family Crystals

PROPERTY	SBN: 75	SBN: 60	BSKNN-2	BSKNN-3	SCNN	PBN: 60
SYMMETRY	4mm	4mm	4mm	4mm	mm2	4mm
T_c (oC)	56	78	169	178	270	300
DIELECTRIC CONSTANT	ε_{33} = 3000 ε_{33} = 700	ε_{33} = 900 ε_{11} = 400	ε_{33} = 170 ε_{11} = 750	ε_{33} = 270 ε_{33} = 800	ε_{33} = 1700 ε_{11} = 1700	ε_{33} = 500 ε_{11} = 1900
ELECTRO-OPTIC COEFF. (x 10^{-12} m/V)	r_{33} = 1400 r_{51} = 42	r_{33} = 420 r_{51} = 60	r_{33} = 200 r_{51} = 450	r_{33} = 300 r_{51} = 500	r_{33} = 1100 r_{51} = 1100	r_{33} = 400 r_{51} = 2400
POLARIZATION (μ Coul/cm^2)	25	33	34	34	35	70
PIEZOELECTRIC COEFF. (x 10^{-12})	d_{33} = 135 d_{15} = 24	d_{33} = 120 d_{15} = 28	d_{33} = 60 d_{15} = 200	d_{33} = 50 d_{15} = 258	—	d_{33} = 100 d_{15} = 300

2.2.1 The SBN System

The solid solution SBN, $0.75 \geq x \geq 0.25$, belongs to the tungsten bronze family, as shown in Fig. 4, even though the end members $SrNb_2O_6$ and $BaNb_2O_6$ do not exhibit a tungsten bronze structure. This system was originally studied at Bell Laboratories where SBN:50 crystals were grown using the Czochralski technique, considering SBN:50 to be the congruent melting composition. In the mid-1970's, Honeywell researchers also studied the growth of doped and undoped SBN:50 for pyroelectric applications with considerable success. Subsequently, Japanese researchers reexamined the phase relation in the $SrNb_2O_6$-$BaNb_2O_6$ system and reported that $Sr_{0.6}Ba_{0.4}Nb_2O_6$ (SBN:60) is the only congruent melting composition in this system. The work at Rockwell International also confirmed that SBN:60 is very close to congruent melting, and therefore is much easier to grow than SBN:50 or SBN:75.

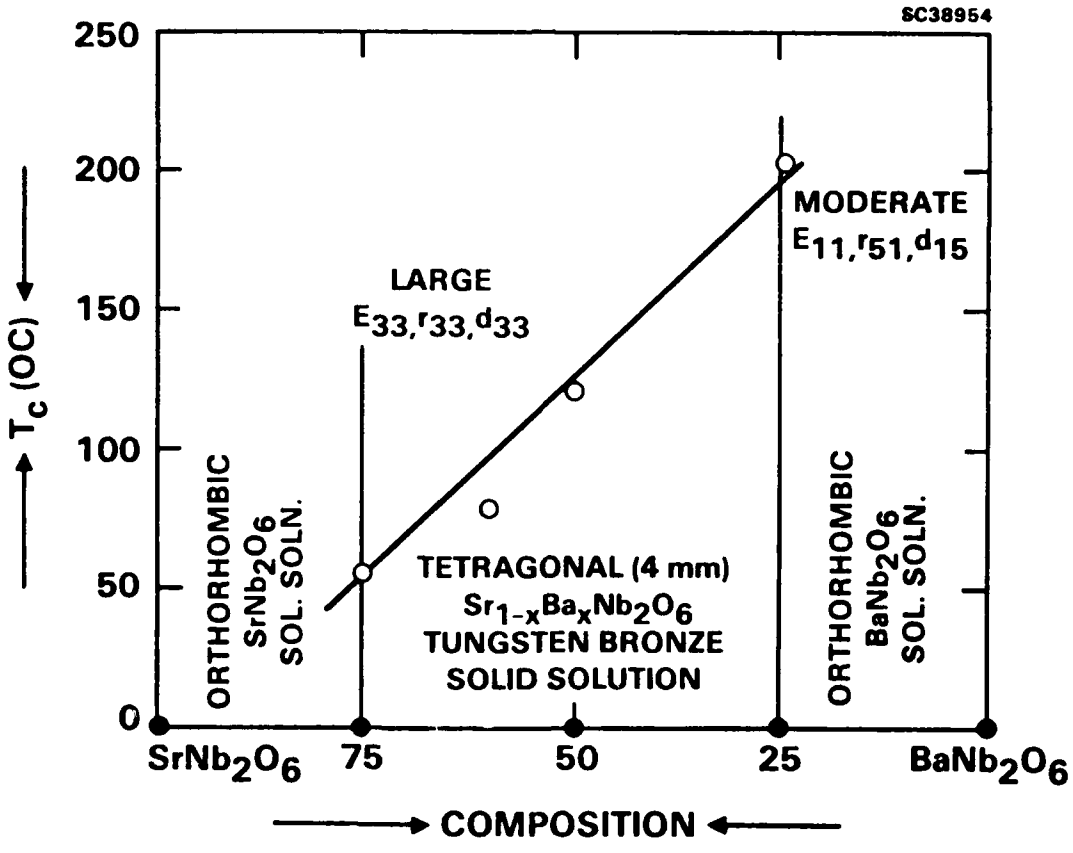


Fig. 4 Curie temperature vs composition for the $SrNb_2O_6$-$BaNb_2O_6$ binary system.

The tetragonal tungsten bronze SBN solid solution is represented by the formula $(A_1)_4(A_2)_2B_{10}O_{30}$ in which both Ba^{2+} and Sr^{2+} are in the 15-fold (A_1) and 12-fold (A_2) coordinated lattice sites. Since the 15- and 12-fold coordinated sites are partially empty in this system, SBN is referred to as an unfilled bronze. Furthermore, because of these partially empty crystallographic sites, both Ba^{2+} and Sr^{2+} have a considerable tendency to exchange sites, often creating crystal strain and optical striations. However, these problems have now been successfully overcome, and optical-quality crystals are now available for SBN:60.[9]

2.2.2 The PBN System

Figure 5 shows the ferroelectric tungsten bronze system $Pb_{1-x}Ba_xNb_2O_6$ in which the MPB region is located at $x = 0.37$.[14] In this region, the electro-optic, pyroelectric, piezoelectric and dielectric properties are exceptionally large and are largely temperature-independent. Several of the more useful tungsten bronze systems show MPBs near which the polarization is large, giving large electro-optic and dielectric properties. As shown in Fig. 5, on a binary phase diagram an MPB appears as a nearly verticle line separating two ferroelectric phases, i.e., the boundary occurs at a nearly constant composition over a wide temperature range up to the Curie temperature. Poled crystals near such a boundary show unique and enhanced electro-optic properties because of the proximity in free energy of an alternative ferroelectric structures. A detailed description of MPB behavior has been provided by Jaffe et al.[15]

In the $Pb_{1-x}Ba_xNb_2O_6$ system, Shrout et al[14] demonstrated that it is possible to grow striated, small size crystals with compositions close to the MPB. For compositions on both sides of the boundary, the g_{ij} quadratic electro-optic coefficients are largely temperature-independent, as expected, and are significantly larger than those for $Sr_{1-x}Ba_xNb_2O_6$ solid solution crystals. With increasing Pb^{2+} content, the piezoelectric coefficients d_{15} and d_{33}, shown in Fig. 6, escalate dramatically as the composition approaches the MPB, with longitudinal values larger than those found for $BaTiO_3$.

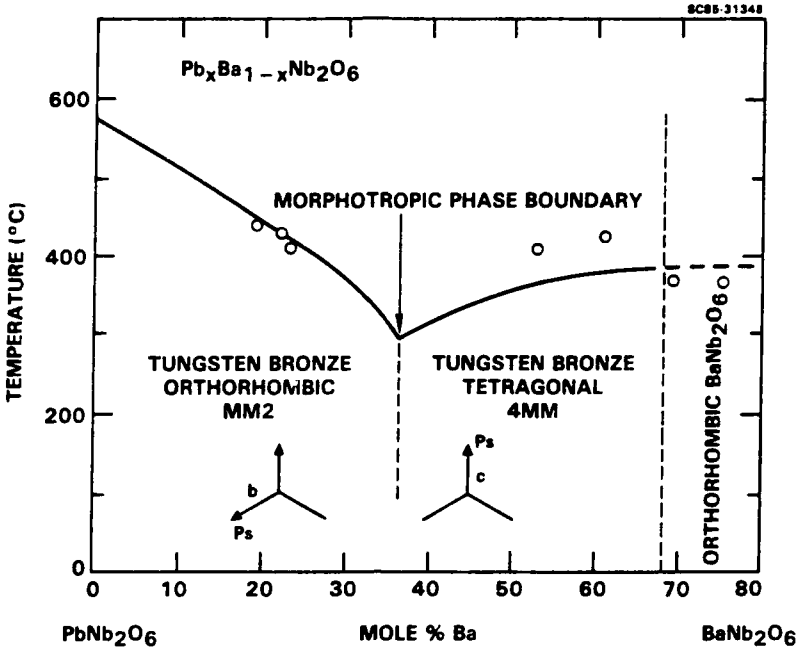


Fig. 5 Curie temperature vs composition for the $PbNb_2O_6$-$BaNb_2O_6$ binary system.

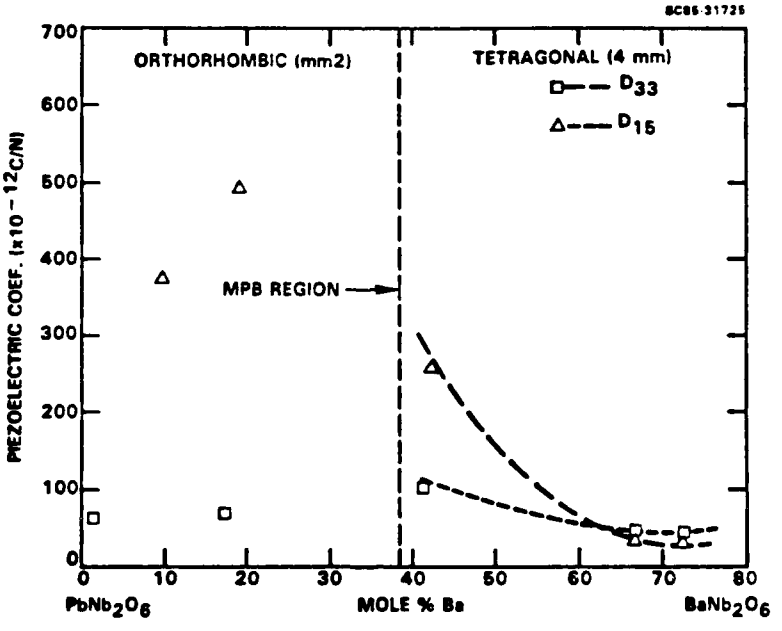


Fig. 6 Piezoelectric d_{33} and d_{15} coefficients as a function of composition in the $PbNb_2O_6$-$BaNb_2O_6$ system.

Two phases exist in tungsten bronze $Pb_{1-x}Ba_xNb_2O_6$: orthorhombic (2 mm) for $x \leq 0.37$ and tetragonal (4 mm) for $x \geq 0.37$. Since the tetragonal composition $Pb_{0.6}Ba_{0.4}Nb_2O_6$ (PBN:60) is close to the MPB, this composition was selected in the present work for thin film growth. As summaried in Table 1, this near-morphotropic composition has a dielectric constant $\epsilon_{11} = 1900$ and an electro-optic coefficient $r_{51} = 2400 \times 10^{-12}$ m/V at room temperature based on previous bulk single crystal measurements.

2.3 Experimental Procedure

The proper preparation of sputtering targets of 3 to 6 in. diameter is important to achieve compositional homogeneity in ferroelectric films. The use of a binder in the starting materials and careful sintering helped to prepare large size targets of the appropriate thickness with high purity carbonates and oxides used as starting materials. The cold-pressed disks were carefully sintered in an oxygen atmosphere above 1200°C and the target compositions were checked by x-ray diffraction measurements.

Single crystals of SBN:60 and BSKNN grown by the Czochralski techniqu were used as substrate materials along with other materials such as sapphire, quartz and glass. These crystals were grown by the Czochralski technique,[9] and in the case of SBN:60 crystals, wafers as large as 1 in. diamater were available for this work. Since tungsten bronze single crystals exhibit natural facets, the orientation of a given crystal, e.g., (001), (100) and (110), was easily achieved.

As shown in Fig. 7, a magnetron sputtering unit was used for film growth. To obtain single crystal or grain-oriented films, it was important that the substrate be at elevated temperatures, preferably around 600°C. As shown in Fig. 7, a substrate hot-stage was incorporated so that the substrate temperature could be changed according to observed film crystallinity and orientation, both of which are influenced by temperature. After evacuation of the chamber to 5×10^{-5} Torr, either argon or argon + oxygen were used for sputtered film growth.

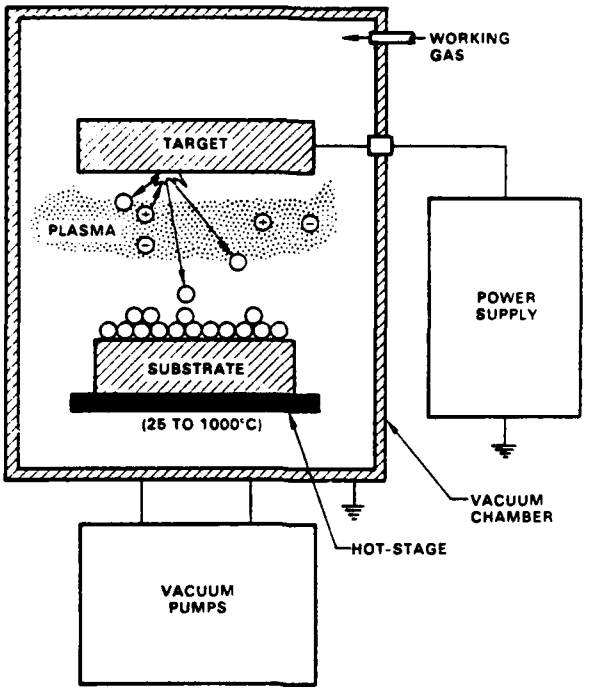


Fig. 7 Schematic representation of the sputter coating process.

2.4 Results and Discussion

The growth of two important tungsten bronze compositions, $Pb_{0.6}Ba_{0.4}Nb_2O_6$ (PBN:60) and $Sr_{0.75}Ba_{0.25}Nb_2O_6$ (SBN:75), was studied in more detail using various substrates growth under different conditions. Since PBN:60 does not exhibit a high symmetry pyrochlore structure as observed in perovskite compositions such as $PbTiO_3$ and PLZT, the development of PBN:60 films with a tungsten bronze structure was greatly simplified. The results of our experiments are summaried in Table 2 along with the following observations:

Figures 8 and 9 show x-ray diffraction patterns for PBN:60 thin films deposited on various substrates such as quartz, Si and SBN:60 (oriented in three different orientations). The growths on these substrates were successful. However, in the case of SBN:75 films, the required annealing temperature was much higher (over 800°C) compared to PBN:60 films, since SBN:75 is a highly refractory material. However, the use of such high annealing temperatures did not affect the surface quality of these films. A brief account of the films grown on various substrates is given in the following sections.

Table 2

Ferroelectric PBN:60 and SNB:75 Films

SBN:60 Substrates	Nonferroelectric Substrates
*Substrate Temperature < 300°C	(MgO, Si, Quartz, Glass) *Substrate Temperature < 300°C
Poorly Crystallized Needed Annealing over > 500°C	Amorphous Films up to 500°C
*Substrate Temperature > 600°C	*Substrate Temperature > 600°C
Well Crystallized Films	Well Crystallized Films over 800°C
Single Crystal Films	Polycrystalline Films
Films Have Excellent Surface Quality	Films Have Good Surface Quality
Films are Ferroelectric	Films are Ferroelectric

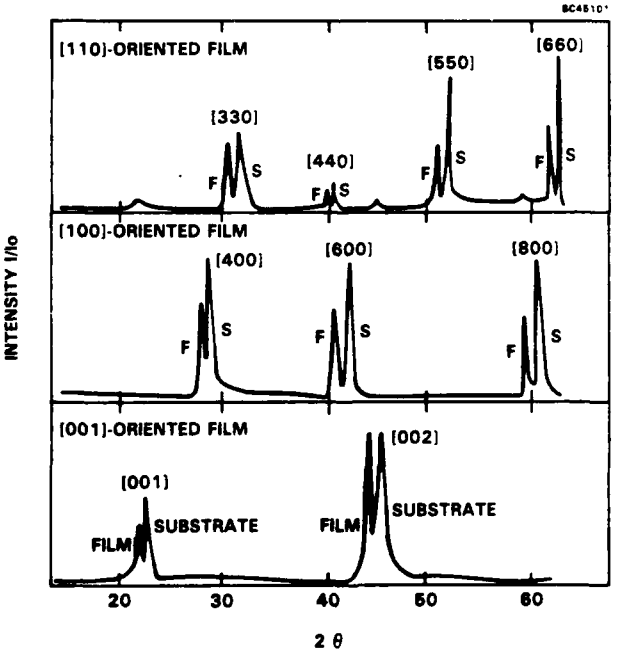


Fig. 8 Tungsten bronze PBN:60 films on [001], [100], and [110]-oriented SBN:60 substates.

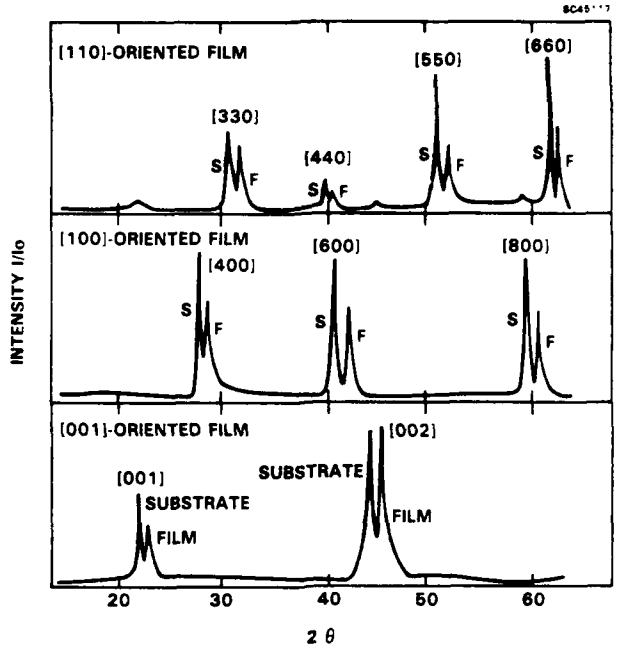


Fig. 9 Tungsten bronze SBN:75 films on [001], [100] and [110]-oriented SBN:60 substrates.

2.4.1 Thin Film Growth on SBN:60 Substrates

Figures 8 and 9 show x-ray diffraction patterns of PBN:60 and SBN:75 thin films deposited on (001), (100) and (110)-oriented tungsten bronze SBN:60 substrates using a single target having a PBN:60 or SBN:75 composition. The growth of these films was successful in all orientations and showed the typical tungsten bronze structure, except for a few extra weak reflections for films grown on (110) substrates. As can be seen from these figures, the epitaxy is generally good and the films are well crystallized. When the films were deposited on (001)-oriented SBN:60 substrates, only the (001) and (002) x-ray diffraction peaks were observed, whereas the reflections corresponding to (400), (600) and (800) were observed when the films were deposited on (100)-oriented SBN:60 substrates. In the case of (110) SBN:60 substrates, lines corresponding to (330), (440) and (660) were dominant and we also found additional reflections in close agreement with the (400) and (600) diffraction peaks. This indicates that orthorhombic (100)-oriented films are present. The tungsten bronze compositions exhibit two structural forms, tetragonal (4 mm) and orhorhombic (2 mm), and they are crystallographically related to one another as follows:

$$\sqrt{2} \cdot a_{Tetra}(\text{i.e. } [110]) = a_{ortho}[100] .$$

This suggests that films deposited on (110)-oriented substrates are metastable and can take either a tetragonal or orthorhombic form. However, the current results are not sufficient to predict under what conditions one form is stable over another. Currently, further experiments using varied substrate temperatures are underway to study the structural transformation behavior on (110) substrates. Recently, Adachi et al[16] demonstrated the growth of tetragonal $K_3Li_2Nb_5O_{15}$ (KLN) on the $a/\sqrt{2}$ substrate (Fig. 10), but did not mention orthorhombic KLN on (001) or (100)-oriented substrates. Based on our current work, it seems possible to stabilize either the tetragonal and orthorhombic forms using (100)-oriented tetragonal substrates and appropriate growth conditions. Since only a few orthorhombic tungsten bronze crystals are known and available, this opens up a new method to obtain orthorhombic bronzes for device studies. In particular, the PBN:60 films grown on either orientation are fully crystallized at 600°C or above with quality sufficient for optical performance.

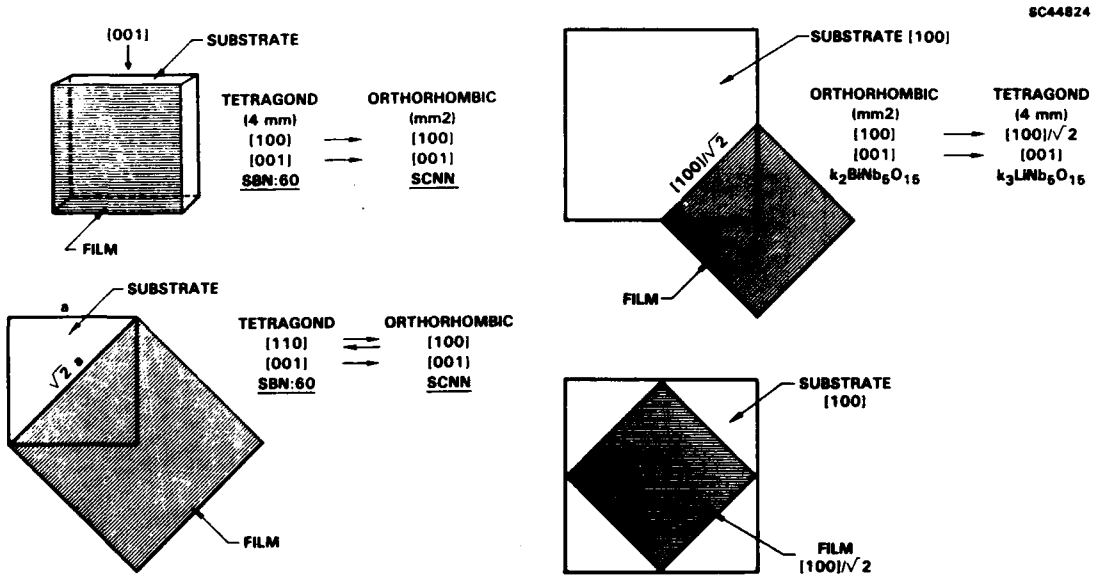


Fig. 10 Crystallographic relation between (mm2) and 4 mm) bronze structures.

Since SBN:75 exhibits excellent transverse electro-optic properties ($r_{33} = 1400 \times 10^{-12}$ m/V), it would be very interesting to test its longitudinal electro-optic properties in the orthorhombic form. The films developed on (100)-oriented SBN:60 substrates show a mixture of orthorhomic and tetragonal SBN:75. Since SBN:75 is refractory, the films were annealed at much higher temperatures (≥ 750°C) compared to PBN:60 films.

The rate of deposition of various orientations was checked and it was found that the crystallization rate is faster along <001>, an observation consistent with our work on bulk single crystals of these compositions[9] which grow only along <001>. As shown in Fig. 11, the intensity of the film peaks was found to increase with film film thickness. Based on our LPE work on SBN and $LiNbO_3$ films, it is important to have film thickness 8 μm or higher to suppress contributions from the substrate. Except for spatial light modulators (SLM), we believe that thicker films are not required for device studies.

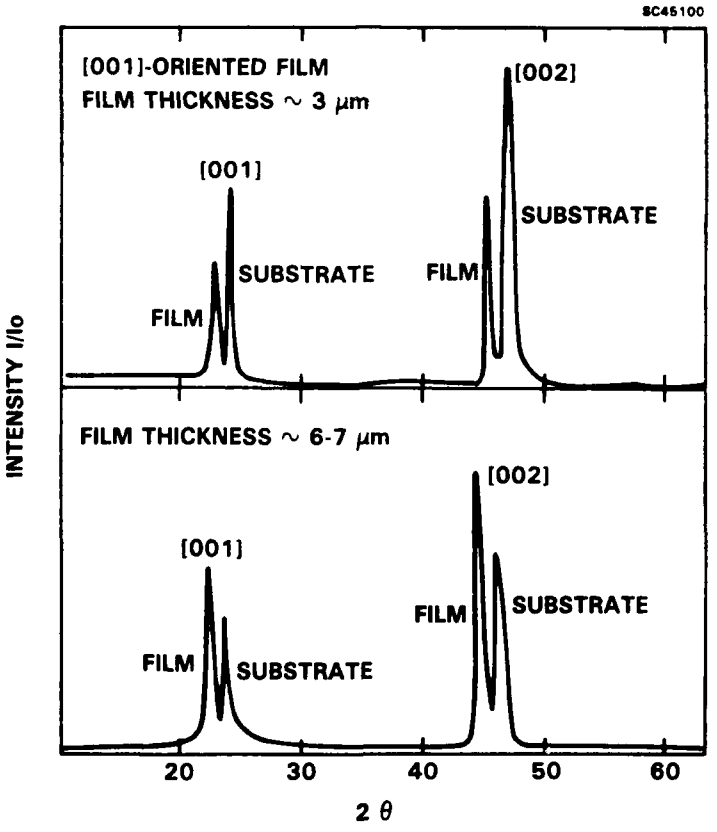


Fig. 11 Intensity as a function of film thickness for PBN:60 films.

The lattice constants established for PBN:60 films using x-ray diffraction data are a = 12.503Å and c = 3.986Å, in close agreement with the target values. This clearly suggests that the film and target compositions are almost the same. However, in the case of SBN:75, the lattice constants are slightly different, indicating a change in the Sr^{2+}:Ba^{2+} ratio. Further efforts are underway to correct this problem by adjusting the target composition.

2.4.2 Thin Film Growth on Nonferroelectric Substates

As shown in Fig. 12, the films grown on nonferroelectric substrates such as glass, quartz, MgO and Al_2O_3 are basically polycrystalline and did not show any evidence of grain orientation. Furthermore, the films were essentially amorphous when the substrate temperature was 600°C or below and required higher annealing temperatures in excess of 700°C. The film quality and surface texture for these films are sufficient for various applications such as pyroelectric detectors, piezoelectric sensors and multilayer capacitors.

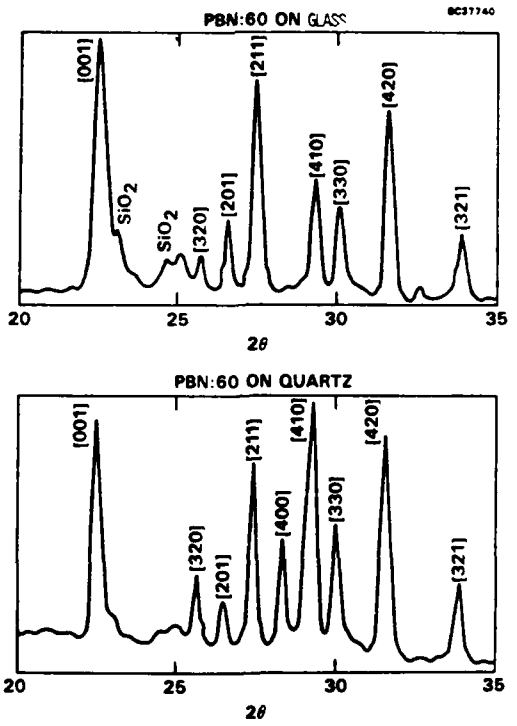


Fig. 12 Tungsten bronze PBN:60 film on glass and quartz substrates.

2.4.3 Thin Film Growth on Semiconductor Substrates

The growth of PBN:60 and SBN:60 films was attempted on semiconductor substrates such as Si and GaAs. As shown in Fig. 13, films grown on Si substrates were essentially polycrystalline with excellent epitaxy up to 550°C. Beyond this annealing temperature, the films peeled off from the substrates due to the large lattice mismatch. In the case of GaAs substrates, annealing has to be performed below 500°C and at these temperatures, the films were poorly crystallized. Although film growths on silicon substrates were successful, their usefulness will depend on the quality and crystallinity of the films. The two major problems are the separation of the films at high temperatures. and the atmosphere under which they are grown. In oxygen, one gets an SiO_2 layer between the film and substrate, whereas in inert conditions, Nb^{5+} shows a great tendency to reduce to Nb^{4+}. For this reason, we are critically studying the growth conditions so that we can get desirable films without the existence of an SiO_2 layer.

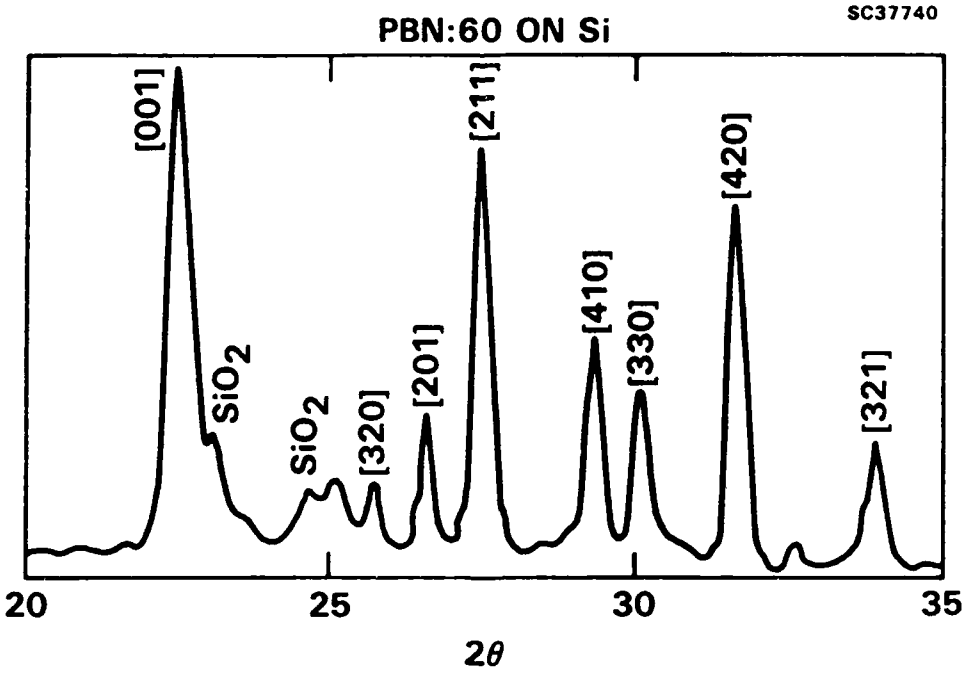


Fig. 13 Tungsten bronze PBN:60 film on [100]-oriented Si-substrate.

2.4.4 Characterization of Ferroelectric Thin Films

We have performed some initial investigations of the dielectric properties of SBN:75 and PBN:60 films grown on quartz substrates using sputtered Pt or Au contacts on the film surface and at the film/substrate interface. The expected dielectric anomalies were observed at the ferroelectric phase transition temperatures of ~ 55°C (SBN:75) and ~ 320°C (PBN:60), but in general the dielectric properties were highly dispersive over the frequency range of 100 Hz-100 kHz, with dielectric loss tangents greater than 10 above 300°C. These results are not surprising in light of the polycrytalline nature of the films; nevertheless, the phase transition temperatures are very close to those for bulk crystals and ceramics, confirming that no major composition change occurred in the growth of either bronze composition.

It is evident at this point that sputtered growth on lattice-matched substrate materials is necessary for good film crystallinity and, therefore, good ferroelectric behavior. However, in the case of SBN:75 thin films, the large transverse optical and piezoelectric properties mandate film growth with the polar axis normal to the film surface. This means that contact metallization, if used, must also be deposited on crystal planes normal to the polar axis for practical device applications, thereby requiring the deposition of a thin metallization layer on the substrate surface prior to thin film growth. This geometry naturally permits very low voltage poling of the film to a single ferroelectric doman and the straightforward evaluation of polar axis dielectric and polarization properties as a function of temperature, but at the possible expense of losing the benefits of lattice matching with the underlying dielectric substrate and, therefore, a loss of film crystallinity. This is an essential question for the utility of SBN:75 thin films, particularly in electro-optic applications, and we are now pursuing the growth of this material on SBN:60 substrates using different types and thicknesses of substrate metallization layers. However, it is worthwhile to piont out that should SBN film growth on n-or p-type semiconductor substrates prove practical, such metallization at the substrate/film interface would then be unnecessary.

Because of the anticipated large longitudinal ferroelectric properties of PBN:60, thin film growth of this material is preferable with the polar c-axis in the plane of the film. Hence, film growth directly on lattice-matched (100) substrates is the ideal geometry for device applications, with contact metallization applied either to the film

edges or on the film surface (Fig. 14). Recently, the electro-optic r_{51} coefficient was evaluated in PBN:60 films deposited on sapphire (Al_2O_3) and with a half-wave voltage of less than 2000 V. We believe that this value will be less than 50 V when film is poled and oriented along the c-axis. Since the film is polycrystalline when grown on sapphire, this present value is considered significantly low. Currently, measurements on PBN:60 and SBN:75 films deposited on SBN substrates are in progress and we believe these films will be appropriate for guided wave optical studies. Since the refractive index difference between PBN:60 (n = 2.410) and SBN:60 (n = 2.240) is large, one can use such structures for guided-wave optics. Optical waveguide devices have been fabricated using $LiNbO_3$ single crystals which, unfortunately, need large operating voltages over 3000 V. If PBN:60 is used in such devices, the requirements for operating voltages will be very low. Next year's effort will be focused on testing the performance of these films for guided wave optics as well as for SLM applications.

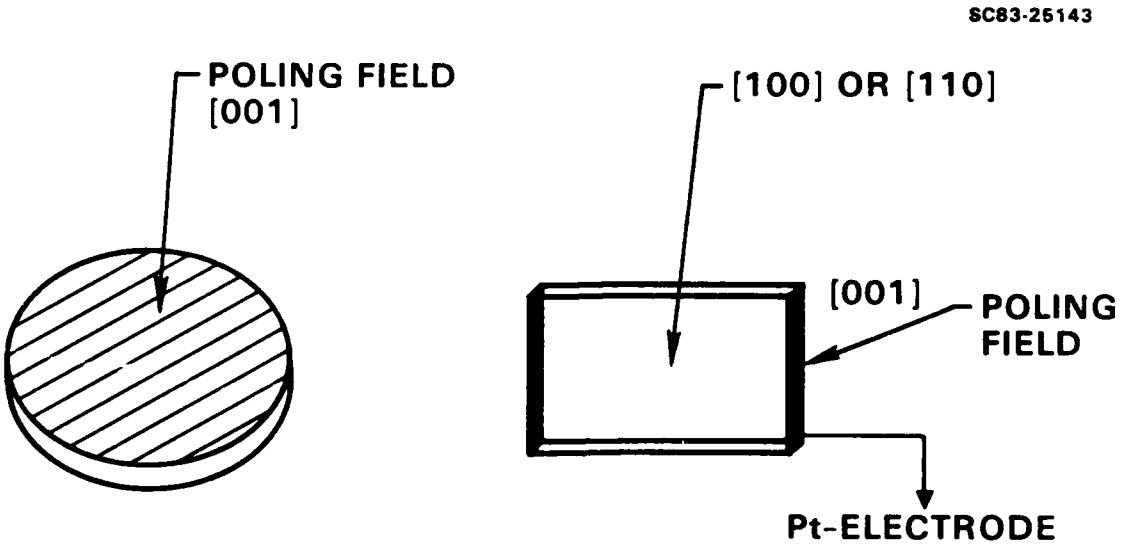


Fig. 14 Poling direction for different ferroelectric film orientations.

2.4.5 Conclusions and Recommendations

The thin film growth of tungsten bronze PBN:60 and SBN:75 has been successful, and films grown on SBN:60 substrates were found to be crystalline. The development of PBN:60 or other Pb^{2+}-containing crystals has historically been frustrated by several problems associated with Pb losses. Hence, the development of PBN:60 thin films is considered an important step for understanding its directionally dependent properties and exploring possible device applications. Since SBN:75 and PBN:60 both exhibit large electro-optic effects, these films have great potential for optical applications such as guided wave optics, photorefractive devices and adaptive optics. The work to date shows that thin film growth is possible in either of two orientations, (001) or (100), to take advantage of optical properties specific to each material. Future work will focus on the following:

1. Establish conditions that stabilize tetragonal and orthorhombic films on (100)-oriented SBN:60 substrates.
2. Examine the ferroelectric and optical properties in films of the same composition but with different structural forms.
3. Attempt single crystal film growth on metallized substrates.
4. Evaluate electro-optic and other ferroelectric properties in PBN:60 and SBN:75 thin films.
5. Establish device concepts and possible limitations using available film characteristics and geometries.
6. Establish multilayer approach if the quality is crucial to device studies.

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3.0 GROWTH OF PEROVSKITE PZT AND PLZT THIN FILMS

GROWTH OF PEROVSKITE PZT AND PLZT THIN FILMS

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ABSTRACT

This paper reports preliminary results on the fabrication of perovskite PZT and PLZT thin films using a sputtering technique. For glass, quartz and sapphire substrates, it was necessary to raise the substrate temperature above 550°C to achieve perovskite tetragonal structures of interest. Growth at temperatures below 550°C yielded a major pyrochlore structure phase. Excess of PbO in target was also required to maintain stoichiometry in these films.

INTRODUCTION

Recently, considerable attention has focused on the development of low-loss ferroelectric thin films for optical waveguides. Several attempts have been made to grow single crystal waveguide films using materials such as $LiNbO_3$,[1-3] PLZT,[4-6] KLN and SBN.[7,8] More recently, other ferroelectric materials such as $BaTiO_3$ and PBN have been considered using semiconductor substrates for various optical applications, including waveguides, spatial light modulators, switches and pyroelectric detectors. The top surfaces of as-grown $LiNbO_3$ and SBN films fabricated by liquid phase epitaxial growth, chemical vapor deposition, melting methods and so on, are relatively rough so that they must be optically polished to couple a light beam into the film. On the other hand, polishing is not necessary for sputtered thin films. Therefore, the sputtering technique has been used in the present work to develop perovskite PZT and PLZT films using a variety of substrates such as glass, quartz and sapphire. This paper reports the growth of PZT and PLZT films and their associated growth problems.

EXPERIMENTAL PROCEDURE

The sputtering targets employed were a mixture of PZT or PLZT and PbO. Approximately 5 mole% excess PbO was added in these targets to control the Pb concentration in the films. The targets were prepared using ceramic sintering or hot pressing; well-mixed powders were cold pressed and then sintered or hot pressed at 1100°C after ball-milling.

Sapphire (Al_2O_3) and quartz (SiO_2) substrates were first etched by sputtering. The substrates were mounted on a heating block with a stainless steel mask of 0.2 mm thickness. Substrate temperature was monitored by a Pt-Pt.Rh 13% thermocouple inserted into the center of the substrate holder. The sputtering conditions, summarized in Table 1 for each material, are as follows:

Target-Substrate Distance:	5 cm
Input Power Density	1.9 to 2.4 W/cm^2
Sputtering Gas	$Ar:O_2$ (40:60 or 50:50)
Gas Pressure	8-12 μm
Substrate Temperature	300-600°C
Deposition Rate	20-25Å/h
Annealing Temperature	700-800°C

EXPERIMENTAL RESULTS AND DISCUSSION

PZT and PLZT compositions have been of practical interest for the last 25 years and are being exploited for optical applications such as switches, modulators, image storage and optical display devices. PZT occurs on the pseudobinary $PbZrO_3$-$PbTiO_3$ system and exhibits a morphotropic phase boundary at a Zr:Ti ratio of 52:48, as shown in Fig. 1. However, the development of bulk single crystals has been hindered by growth problems associated with Pb^{2+} losses during growth and cracking when cycling through the paraelectric/ferroelectric phase transition. For this reason, thin-film growth of these compositions is now being explored in several countries.[9-11]

The deposition of PZT and PLZT films by the sputtering technique has shown that the structure of the film is sensitive to the substrate temperature (Fig. 2). PZT or PLZT thin films having a pyrochlore structure were obtained below 550°C, whereas a perovskite structure was obtained above 600°C. However, traces of $PbTi_3O_7$ were observed with Pb^{2+} deficiencies, and for this reason, an extra 5 mole% PbO was incorporated in the targets to stabilize the film composition.

Figure 3 shows the x-ray diffraction patterns of PLZT films sputtered on fused quartz and sapphire and for a PLZT(9/65/35) hot-pressed ceramic. In Fig. 3, (a) is for a film (~ 4 μm thickness) sputtered at a substrate temperature of 550°C with a target containing 5 mole% of PbO excess, (b) is for a film sputtered at 600°C with a target containing 3 mole% PbO excess, and (c) is for the hot-pressed PLZT ceramic target. The good agreement between the thin film and ceramic target patterns shows that the films have maintained the desired perovskite structure, although they are polycrystalline due to the poor lattice match with the substrates. A small split of the (200) peak into (200) and (002) was observed after a post-growth anneal at 700°C/2 h, indicating a tetragonal symmetry. However, this caused some loss of Pb^{2+}, as indicated by the appearance of small second phase peaks associated with ZrO_2. To maintain a perovskite phase during growth, substrates were held at 600-650°C; growth temperatures below 350°C resulted in completely amorphous films which could not be annealed to a crystalline form. Although excess PbO is clearly required to maintain film stoichiometry during growth, based on evidence from this work and the results of others,[1] the optimum excess PbO amount still needs to be established.

FUTURE PLANNED WORK: MULTILAYERED FERROELECTRIC FILMS

Recent work by Higuma et al[12] has shown that the growth of PLZT single crystal films is possible using perovskite $SrTiO_3$ substrates at temperatures between 500 and 700°C. Although film growth was successful, there was a considerable lattice mismatch between the film and the substrate. Table 2 summarizes the lattice match of PLZT with $SrTiO_3$ and other ferroelectric crystals, including tungsten bronze SBN and PBN. The lattice match between PLZT and PBN is very good for (001)-oriented PBN and potentially allows the growth of better quality PLZT films. In future work, we propose to develop PZT and PLZT films as follows:

1. SBN:60 substrate with a 5 μm PBN:60 film for lattice matching to PZT or PLZT.
2. SBN:60 substrate with a 5 μm PBN:60 film and then alternate PLZT and PBN layers to develop a superlattice structure.

Since the lattice mismatch between PLZT and PBN is small, we expect that optical-quality PZT/PLZT films or PLZT-PBN superlattices can be more readily achieved with these film structures. An additional advantage is the ability to improve the lattice match by adjustment of the Pb:Ba ratio in PBN and thereby improve PZT/PLZT film crystallinity.

The previously discussed considerations for the electrical evaluation of PBN:60 thin films also apply here in the case of PZT/PLZT films. Because of the additional complexity of PZT/PLZT thin-film growth, the growth of good

quality films on metallized substrates may be vastly more difficult than for PBN:60. A closely spaced surface electrode configuration appears to be a preferable geometry for electrical characterization of PZT/PLZT films, at least in the near term. A high-temperature sample holder to accommodate this type of geometry for dc conductivity, pyroelectric and dielectric measurements over a wide temperature range is now being designed and tested for this purpose.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Fig. 1 Morphotropic phase boundary in the PZT system.

Fig. 2 Structural sensitivity of PZT and PLZT compositions.

Fig. 3 X-ray diffraction patterns of PLZT sputtered films and hot-pressed ceramic. (a) Film sputtered with a target with 5 mole% excess PbO; (b) film sputtered with a target with 3 mole% excess PbO; and (c) hot-pressed ceramic.

Table 1

Growth Condition for PZT and PLZT Films

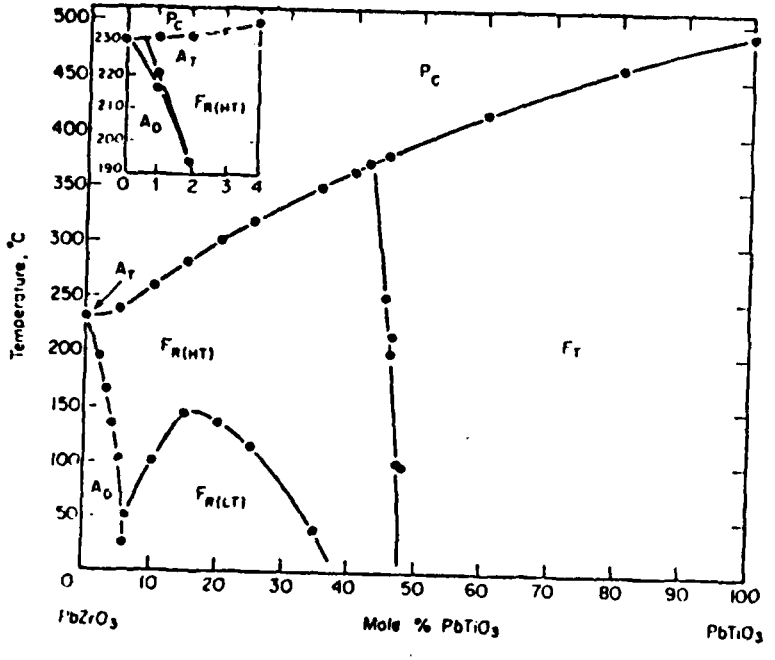
Substrate	Substrate Temperature ≤ 550°C	~ 600°C	Atmosphere	Power Density (W/cm^2)	Film Thickness (μm)	Remarks
PZT Films						
Glass	Pyrochlore	Perovskite	50% Ar + 50% O_2	2.2-2.4	1-5	
Quartz (SiO_2)	Pyrochlore	Perovskite	50% Ar + 50% O_2	2.2-2.4	3-10	Excellent Films
Sapphire (Al_2O_3)	Pyrochlore	Perovskite	50% Ar + 50% O_2	2.2-2.4	3-10	Reasonable Quality
PLZT Films						
Glass	Pyrochlore	Perovskite	40% Ar + 60% O_2	1.9-2.1	3-10	Reasonable Quality
Quartz (SiO_2)	Pyrochlore	Perovskite	40% Ar + 60% O_2	1.9-2.1	2-8	Excellent Quality
Sapphire (Al_2O_3)	Pyrochlore	Perovskite	40% Ar + 60% O_2	1.9-2.1	2-5	Reasonable Quality

Table 2

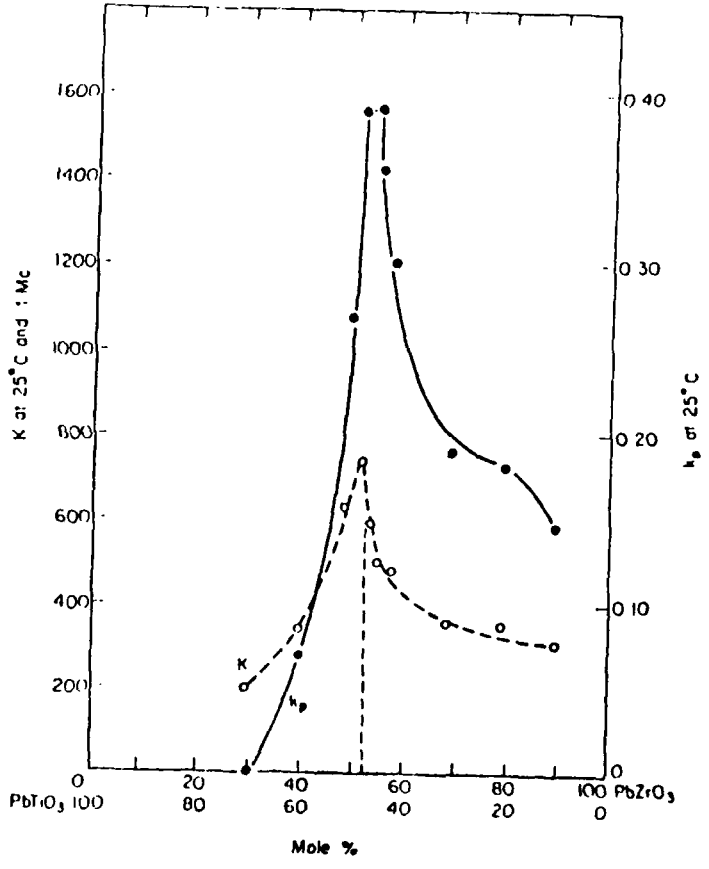
Lattice Match Between PZT/PLZT and Tungsten Bronze Substrates

Film Composition	(001)-Oriented Tungsten Bronze Substrates			Perovskite
	SBN:60	BSKNN	PBN:60	$SrTiO_3$
PZT (40:60)				
a = 4.042Å	2.6%	1.99%	1.4%	3.01%
c = 4.082Å	3.6%	3.00%	3.00%	4.12%
PLZT (8/40/60)				
a = 4.029Å	2.1%	1.5%	1.1%	2.5%
c = 4.072Å	3.4%	2.7%	2.1%	4.3%
PBN:60				
a = 12.501Å	0.38%	0.20%	-----	-----
c = 3.985Å	0.65%	0.35%	-----	-----

MORPHOTROPIC PHASE BOUNDARY IN PZT SYSTEM



(a)



(b)

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Science Center

FIGURE 1

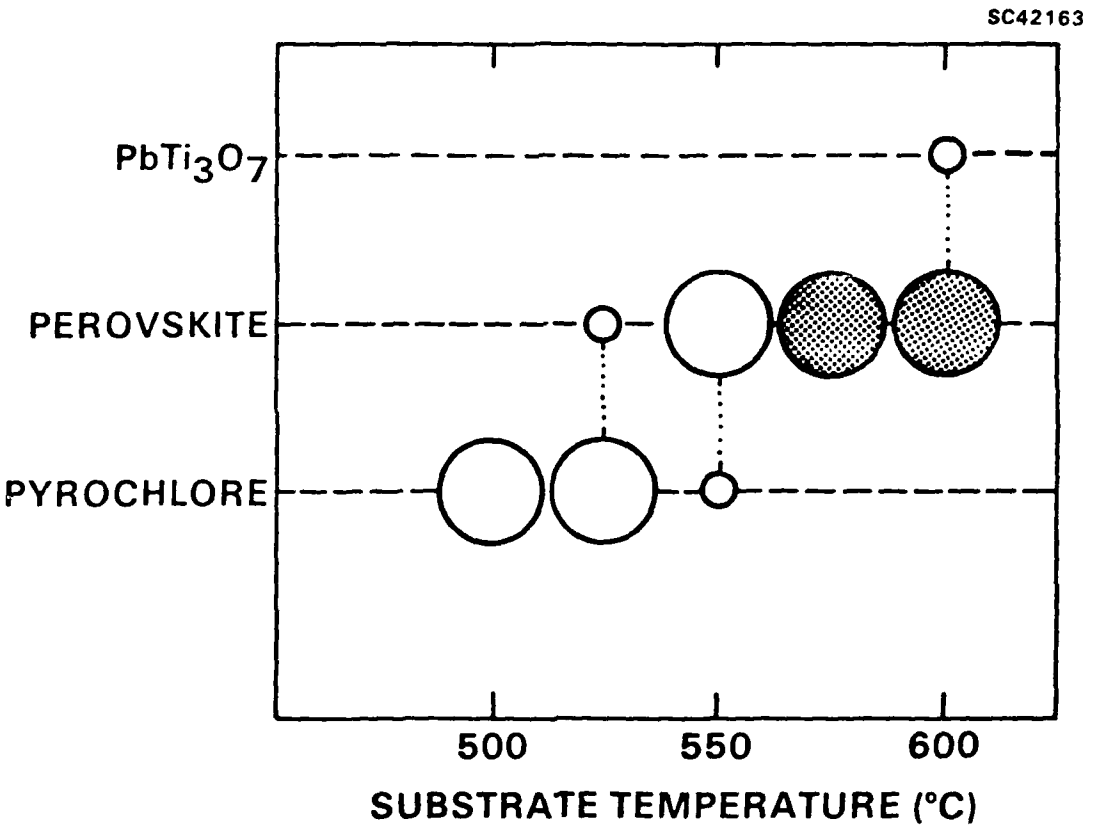
SC42163
$PbTi_3O_7$
PEROVSKITE
PYROCHLORE
500
550
600
SUBSTRATE TEMPERATURE (°C)

FIGURE 2

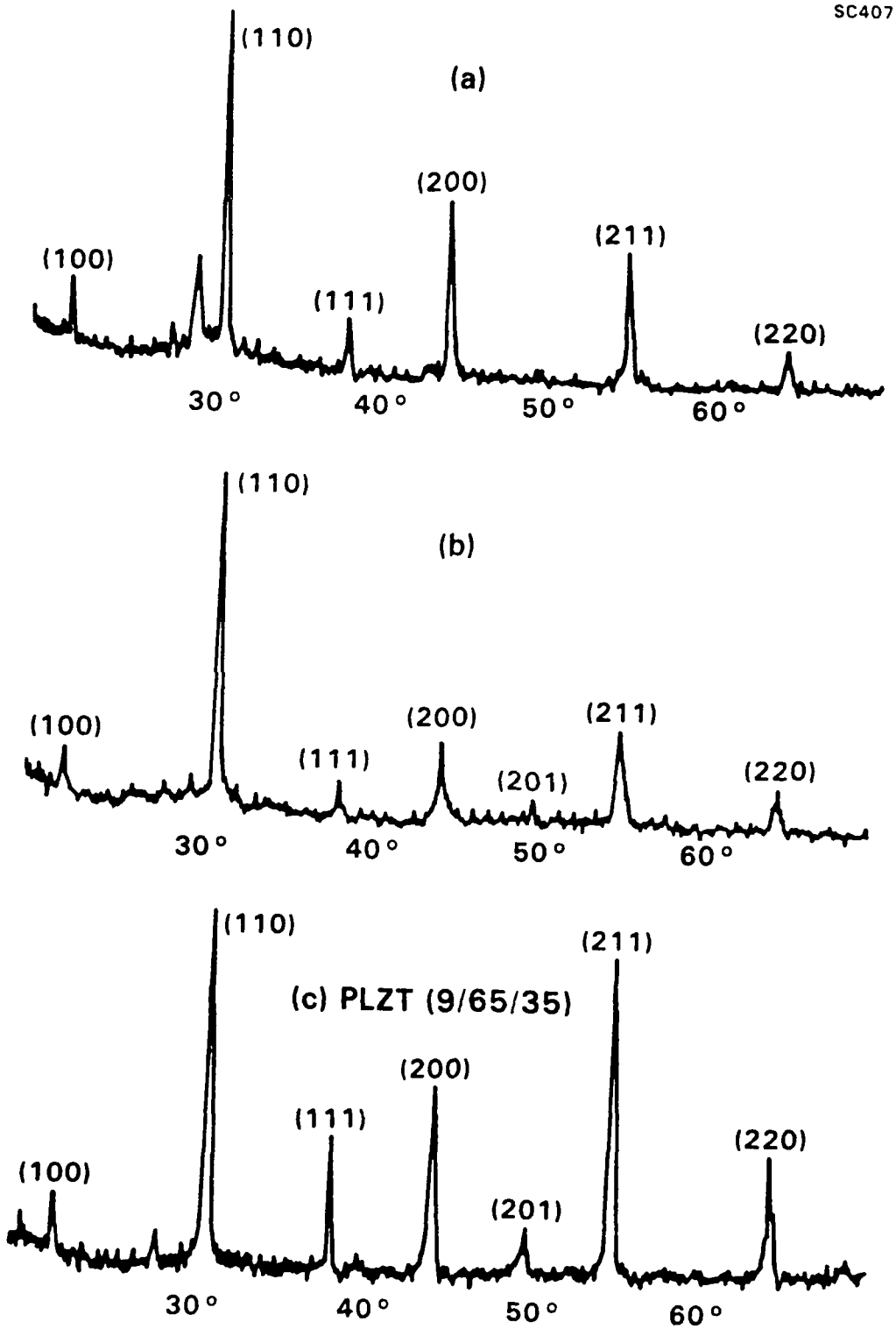
SC40776
(110)
(a)
(200)
(211)
(100)
(111)
(220)
30°
40°
50°
60°
(110)
(b)
(100)
(200)
(211)
(111)
(201)
(220)
30°
40°
50°
60°
(110)
(211)
(c) PLZT (9/65/35)
(200)
(111)
(220)
(100)
(201)
30°
40°
50°
60°

FIGURE 3

4.0 EPITAXIAL GROWTH OF PLZT SINGLE CRYSTAL FILMS ON BRONZE SBN SUBSTRATES BY THE SPUTTERING TECHNIQUE

EPITAXIAL GROWTH OF PLZT SINGLE CRYSTAL FILMS ON BRONZE SBN SUBSTRATES BY THE SPUTTERING TECHNIQUE

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ABSTRACT

This paper reports the preliminary results of epitaxial growth of single crystal PLZT thin films on tungsten bronze $Sr_{0.6}Ba_{0.4}Nb_2O_6$ (SBN:60) substrates by the rf sputtering technique. The films were deposited primarily with (100) SBN substrate orientation and temperatures over 500°C. These films exhibit excellent epitaxy with film orientation along the (100) direction. A multilayer approach has been proposed to improve film quality and properties.

INTRODUCTION

A lanthanum-modified lead-zirconate-titanate solid solution system (PLZT) is a well known ferroelectric material. PLZT is transparent in the visible and near-infrared regions, has various electro-optic[1] and photochromic[2] activities, and promises excellent optoelectronic properties. There have been numerous concepts for its application in electronic and optoelectronic devices making use of these interesting properties, e.g., in a nonvolatile FET memory with ferroelectric gates;[3,4] optical switches;[5] image storage;[6] optical modulators;[7] and, optical display devices.[8] Considerable practical interest has been generated on a PLZT thin films for the purpose of reducing the drive voltage, miniaturization and cost reduction of optoelectronic devices.

Quite recently, several attempts to prepare a PLZT thin films have been initiated using rf sputtering and electron beam evaporation,[9-12] and some PLZT thin films possessing good ferroelectric properties have been obtained. However, from the viewpoint of applications in optical waveguide systems, the preparation of better thin films with high transparency in required. The most significant obstacle in obtaining good transparency and electro-optic properties is the difficulty in growing the perovskite structure with large grain size on suitable substrate materials during film deposition and heat treatment, since the grains increase absorption due to light scattering. We have conducted a series of experiments on the epitaxial growth of PLZT thin films on single crystal tungsten bronze $Sr_{0.6}Ba_{0.4}Nb_2O_6$ (SBN:60) substrates and have succeeded in growing these films with good crystallinity. In this paper, the growth of these thin films, their structural properties, and their applicability to electro-optic devices in integrated optics are discussed.

Experimental Procedure

The sputtering targets employed were a mixture of PLZT and PbO. Approximately 5 mole% excess of PbO was added in the targets to control the Pb^{2+} concentration in the films. The targets were prepared using ceramic sintering or hot-pressing; well-mixed powders were cold pressed and then sintered or hot-pressed at 1000°C after ball-milling. The Zr:Ti ratio was 45:55 and the La^{3+} concentration varied between 2 to 5 mole% in these targets. The targets thus prepared showed no extra phases and were fabricated in 3 in. diameters to obtain uniform film deposition.

The PLZT thin films were deposited with an MRC rf sputtering instrument; the sputtering conditions are summarized in Table 1. SBN:60 crystal substrates of dimensions 10 × 10 × 1 mm were cut in the (001) plane. Some of the substrates were polished to optical quality, etched with HF acid after polishing, or mechanochemically polished. The substrate temperature was maintained between 100 to 500°C during these film growths.

RESULTS AND DISCUSSION

The epitaxial growth of PZT and PLZT has been subject of great interest for various applications, with film growth proving successful on various substrates (MgO, Si, SiO_2, Al_2O_3, Pt, glass, etc.). However, the films obtained on these substrates are basically polycrystalline, with frequent occurrences of a pyrochlore phase. Recently, Higuma et al[14,15] grew PLZT films on $SrTiO_3$ substrates and reported that the films were single crystal with excellent epitaxy. $SrTiO_3$ is cubic at room temperature with a lattice constant a = 3.905Å, while PLZT can be either rhombohedral or tetragonal, depending upon the Zr:Ti ratio. The lattice constants for the tetragonal PLZT solid solution are a = 3.904 to 4.05Å

and c = 4.05 to 4.15Å. Thus, one can adjust the film composition such that there is a good lattice match with the substrate. In the present work, we have employed tungsten bronze SBN:60 substrates which are tetragonal at room temperature with lattice constants a = 12.468Å and c = 3.938Å.[16] The PLZT composition selected for epitaxial growth was $Pb_{0.97}La_{0.03}Zr_{0.45}Ti_{0.55}O_3$ (3/45/55) with lattice constants a = 3.955Å and c = 4.125Å. This composition has an excellent lattice match with SBN:60 substrates in the following two orientations:

$$(100)_{film} = (001)_{sub.} \qquad [a_{film} = c_{sub}]$$

$$3 \times (001)_{film} = (100)_{sub.} \qquad [3 \times c_{film} = a_{sub}]$$

As shown in Fig. 1, 3 cm diameter, 7 cm long SBN:60 single crystals of optical quality were used in these growths.[17,18] Two other tungsten bronze crystals having slightly bigger lattice constants, SBN:50 and BSKNN-1, are also available for use as substrates.

PLZT thin films were deposited on (001)-oriented SBN:60 with substrate temperatures varied between 100 and 500°C. As summarized in Table 1, all films were grown in an $Ar:O_2$ atmosphere. The sputtering conditions were as follows:

Target-Substrate Distance:	4-5 cm
Input Power Density:	1.9 to 2.4 W/cm^2
Gas Mixture:	$Ar:O_2$ (50:50)
Substrate Temperature:	100 to 500°C
Deposition Rate:	50-100Å/hr
Annealing Temperature:	600-650°C

Figure 2 shows x-ray diffraction patterns of PLZT thin films deposited on glass and SBN:60 substrates and annealed at 600°C. All of the tetragonal perovskite peaks of PLZT were observed when the film was deposited on glass, with the formation of the pyrochlore phase below 600°C. This result is consistent with work reported by various researchers, including our earlier work.[5-15,19] However, when the film was deposited on the (001)-oriented SBN:60 substrates, only the (100) and (200) diffraction peaks of the film were observed. This clearly shows that the PLZT films deposited on SBN substrates are single crystal with excellent epitaxy. We believe that this is the first time such perovskite films have been grown on tungsten bronze substrates.

The growth of PLZT films was investigated at various substrate temperatures and it was found that the films grown below 400°C were weakly crystallized and needed subsequent annealing above 500°C. However, films grown at substrate temperatures of 500°C or above were well crystallized, single crystal films. Furthermore, the use of SBN substrates completely suppressed the formation of the pyrochlore PLZT phase even at lower temperatures. On the other hand, PLZT films grown on other substrates such as glass, Pt, Al_2O_3 and quartz always exhibited a pyrochlore phase and required high-temperature annealing to convert to the perovskite phase.

The occurrence of a pyrochlore phase is a subject of great interest in Pb^{2+}-containing perovskites and it usually appears when the unit cell c/a ratio is below 1.06, as shown in Fig. 3. Since c/a for $PbTiO_3$-$BiFeO_3$ is 1.17, one does not observe the pyrochlore phase on this system. On the other hand, the pyrochlore phase is found for all compositions in the $PbTiO_3$-$PbZn_{0.33}Nb_{0.66}O_3$ system. The latter is exceptionally important for electro-optic and piezoelectric applications because it exhibits both electro-optic and piezoelectric coefficients very large with a large spontaneous polarization.

The lattice constant a is estimated to be 3.955Å in the PLZT films, in close agreement with the ceramic target value. Electron diffraction patterns need to be studied to ascertain the single crystallinity and polar direction in these films. PLZT deposited on SBN:60 substrates are completely transparent in the visible, cutting off in the IR because of substrate absorption. According to work by Okuyama et al,[15] PLZT films deposited on MgO and $SrTiO_3$ are transparent from the visible to the near-IR. Optical measurements on their films suggest that the optical loss is about 6 db/cm, which is slightly higher than that of $LiTaO_3$ single crystals. However, the half-wave voltage is about one fourtieth of that for $LiNbO_3$, and the reduction of the element size would compensate for the large loss factor. We suspect that this loss can be suppressed further by using well matched substrates such as SBN:60 or other bronze materials.

FUTURE PLANNED WORK: MULTILAYER THIN FILMS

Since the growth of single crystal PLZT thin films on SBN:60 has been successful, it opens up various ways one can improve film quality. If the optical quality or optical loss remains a problem for device applications, a multilayer approach may be appropriate for these films. Since tungsten bronze $Pb_{0.6}Ba_{0.4}Nb_2O_6$ (PBN:60) has a c lattice constant close to the a constant of PLZT, a possibility is to first deposit a PBN:L60 layer on an SBN:60 substrate and then deposit the PLZT film on this layer. Figure 4 summarizes our experimental approach for this concept. As shown in the figure, additional layers of PBN:60 and PLZT may be deposited to improve the film quality of the final film layer. For spatial light modulators and guided wave optics, it is advantageous for the films to have an optical refractive index larger than the substrate, while still maintaining a large optical figure-of-

merit, r_{ij}/ϵ. As shown in Fig. 4, PLZT possesses a significantly larger index than tungsten bronze materials, with Δn of around 0.10.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Fig. 1 SBN:60 singhle crystals grown along <001>.

Fig. 2 Perovskite PLZT thin films on tungsten bronze SBN:60 substrate.

Fig. 3 The c/a ratio for perovskite materials.

Fig. 4 Advantages of multilayer ferroelectric thin films.

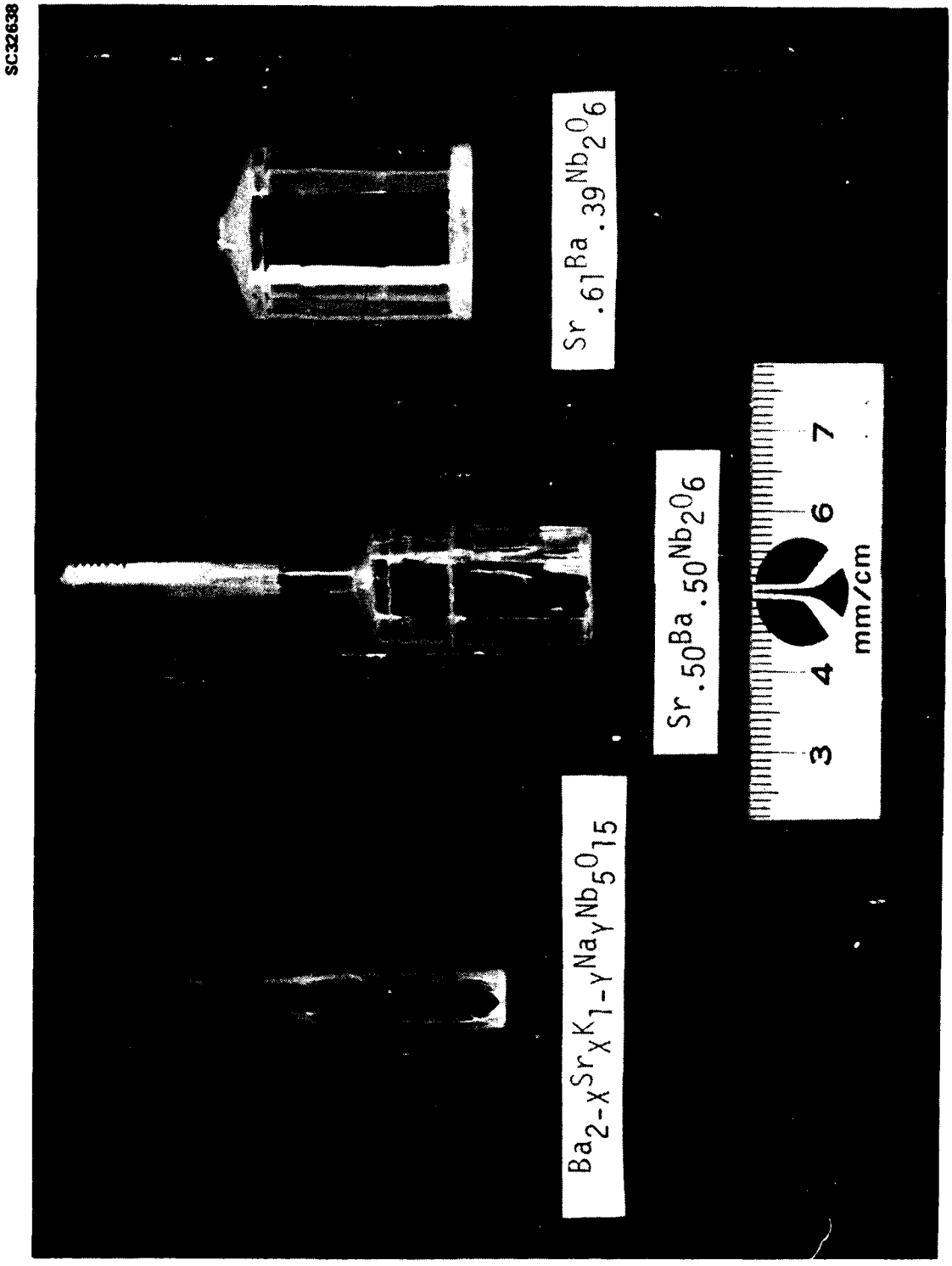


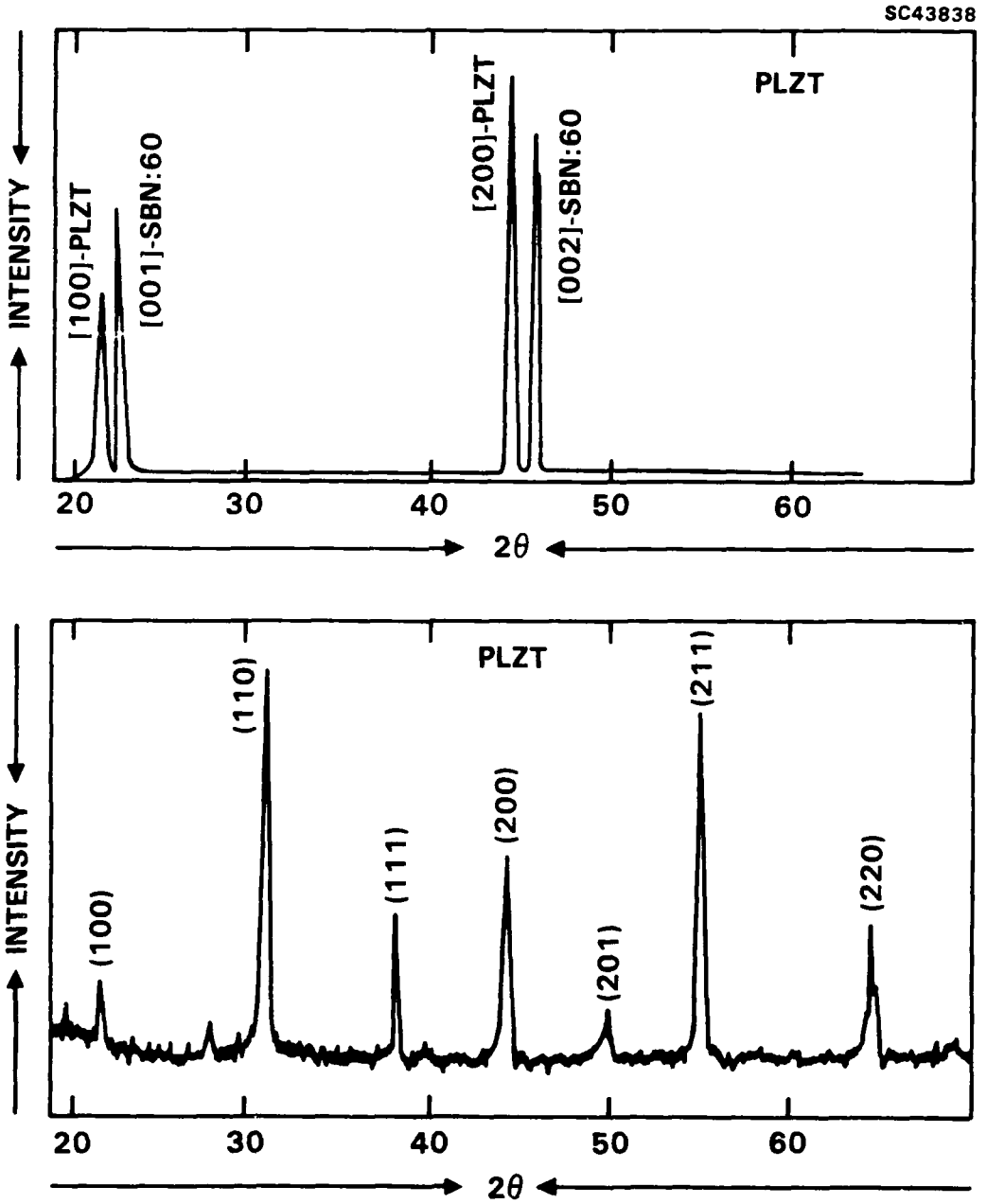
Fig. 1 Czochraski grown SBN and BSKNN bulk single crystals.

Table 1

Growth of PLZT Thin Films on SBN Substrates

PLZT Film	Lattice-Match	As-Grown	Annealed Above 600°C	Lattice Constant	Remarks
(001)-oriented SBN:60 (substrate)					
≤ 400°C	0.40%	Weakly crystallized	Single crystal film	3.953Å	Excellent quality
≥ 550°C	0.40%	Well crystallized	Single crystal film	3.957Å	Excellent quality
Glass-Substrate					
≤ 400°C	--	Amorphous	<600°C pyrochlore >500°C perovskite	a = 3.961Å	Pyrochlore phase problem
≥ 550°C	--	Weakly crystallized pyrochlore	600°C perovskite (polycrystalline)	c = 4.121Å	
Lattice Constants:	SBN:60	a = 12.458Å,	c = 3.938Å		
	PLZT	a = 3.955Å,	c = 4.125Å		

PEROVSKITE PLZT THIN FILMS ON T.B. SBN SUBSTRATES



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LEAD TITANATE-BISMUTH FERRITE

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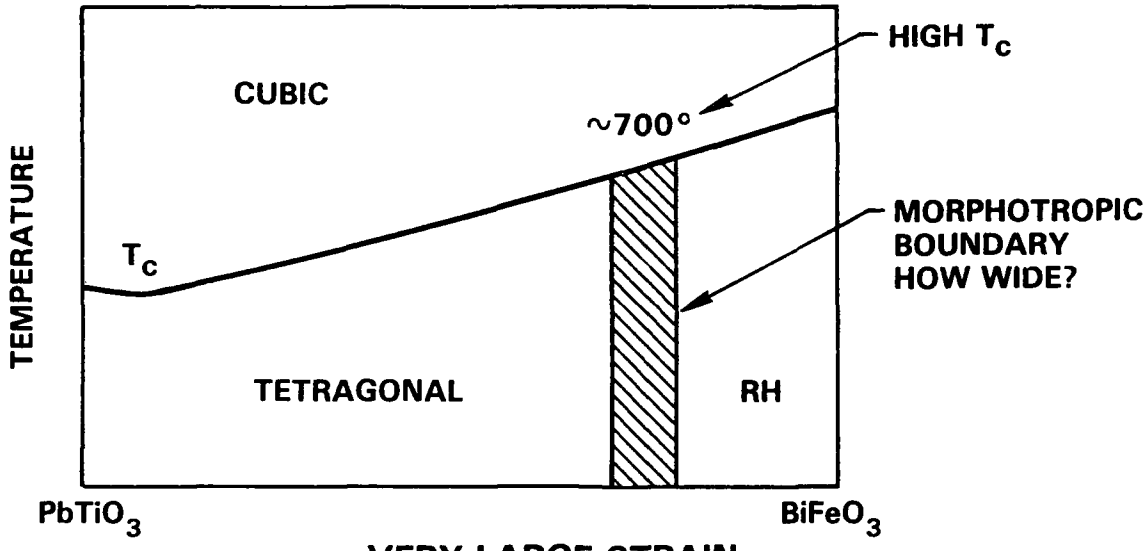
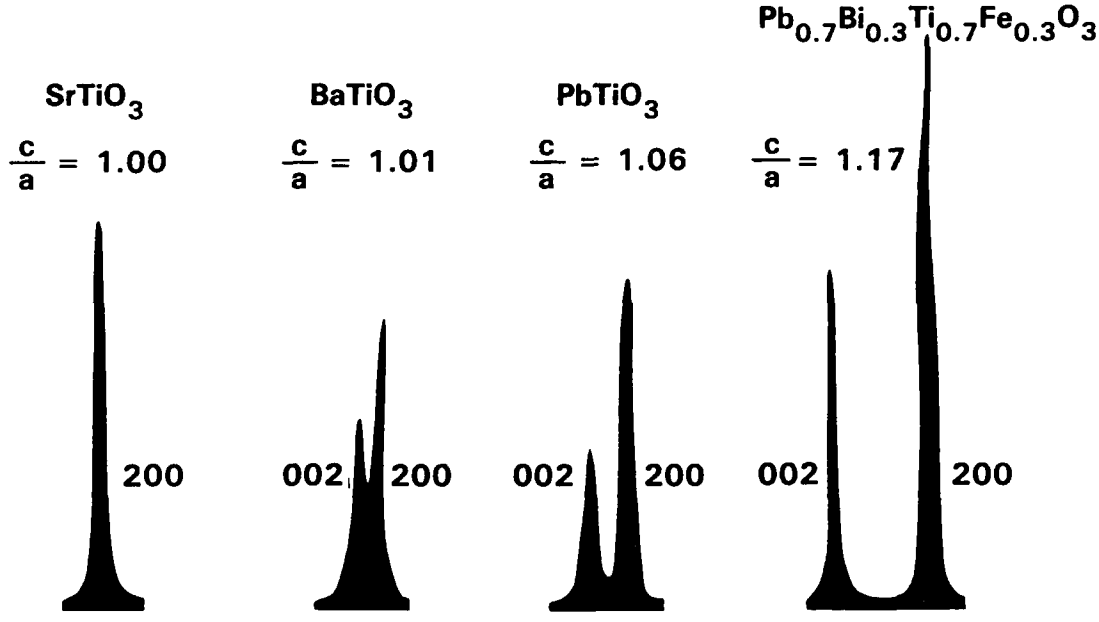


VERY LARGE STRAIN



X-RAY (200) PEAKS

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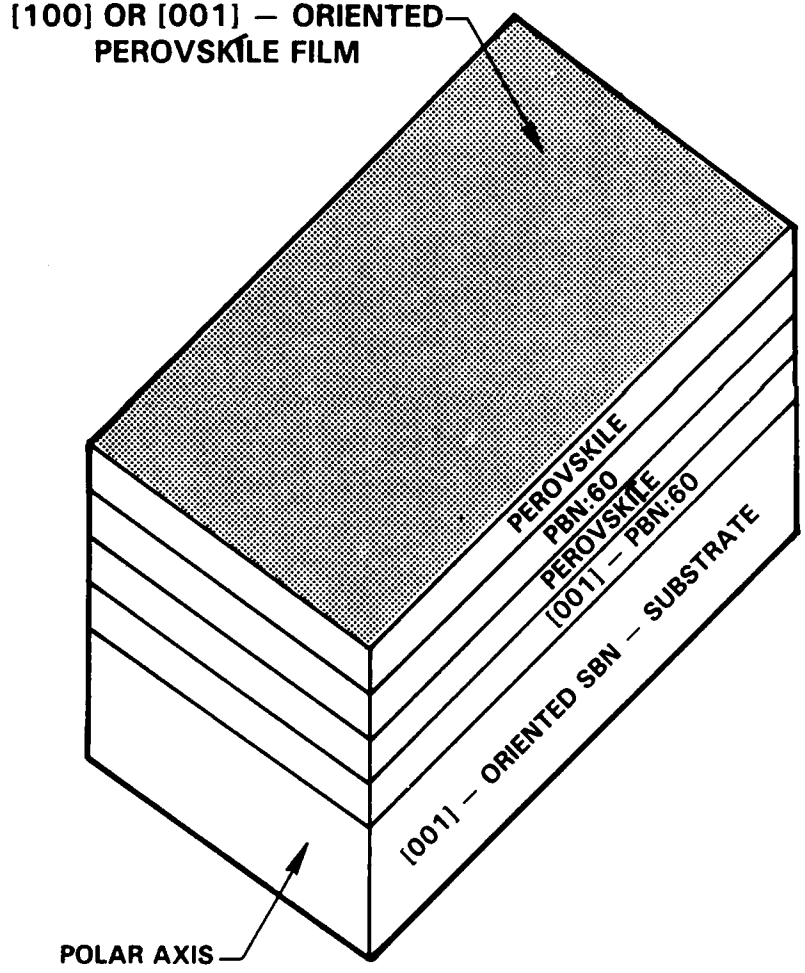
ADVANTAGES OF MULTILAYER FERROELECTRIC THIN FILMS



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SBN:60	PBN:60	PEROVSKILES
[001]	[001]	[100] OR [001]
n = 2·24	n = 2·32	n = 2·4 TO 2·76
LARGE r_{33}, ε_{33}	LARGE r_{51}, ε_{11}	LARGE r_{51}, ε_{33}
T_C = 78°C	T_C = 280°C	T_C = 100 – 300°C

PEROVSKILE FILMS

PZT, PLZT, PZNT, PBFT

APPLICATIONS

- OPTICAL WAVEGUIDES AND SWITCHES
- 3-D STORAGE AND DISPLAY
- PYROELECTRIC AND PIEZOELECTRIC
- MULTILAYER CAPACTITORS

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5.0 INTERIM RESEARCH PROGRESS AND FORECAST REPORT [NOV. 1987]

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November 24, 1987 In Reply Refer To: SC87-1147
SC5458.RPFR

Air Force Office of Scientific Research
Directorate of Electronic and Material Sciences
Building 410, Room 219
Bolling AFB, DC 20332-6448

Attention: Captain Kevin Malloy

Subject: Research on Sputtering of Ferroelectric Thin Films
Research Progress and Forecast Report No. 2
Contract No. F49620-86-C-0052
Project No. 2306/B2
For the Period 01/01/87 to 10/31/87

In accordance with the requirements stated for Contract No. F49620-86-C-0052, following is Research Progress and Forecast Report for the period 01/01/87 to 10/30/87.

The objective of the current program is to understand the factors which control the crystallinity, property, quality and microstructure of sputtered ferroelectric thin films.

Since the inception of this research program in April 1986, considerable progress has been made in producing and characterizing tungsten bronze and perovskite ferroelectric films. Several tasks have been accomplished successfully which are briefly described below.

A. Installation of Sputtering Unit - The key to our research on ferroelectric film growth is the use of specialized equipment for the sputtering of high figure-of-merit ferroelectrics. In order to improve film crystallinity, we recently raised the substrate temperature up to 600°C. Further improvements are under way to achieve higher temperature (above 800°C) using this hot-stage.

B. Materials Selection - Since tungsten bronzes such as $Pb_{1-x}Ba_xNb_2O_6$ (PBN) and $Sr_{1-x}Ba_xNb_2O_6$ (SBN), and perovskite PZT and PLZT are important classes of ferroelectrics for various applications such as photo-refractive, integrated optics, pyroelectrics and piezoelectrics, the development of these ferroelectrics

has continued using the sputtered growth technique. Although Pb^{2+}-containing ferroelectrics are often difficult to obtain in single crystal form due to several growth problems, the growth of epitaxial thin films using SBN:60 substrates has proven highly promising for these materials.

C. Growth of PZT and PLZT Films - The deposition of PZT and PLZT films by the sputtering technique has continued on various substrates including quartz, glass and Si, and we have found that the structure is sensitive to the substrate temperature (Figure 1). PZT and PLZT thin films having a perovskite structure were obtained when the growth or annealing temperature was above 600°C. Below this temperature, the pyrochlore phase was predominant. Deposition on Si substrates has been tried in our work as well as in Japan with considerable success, but the films are polycrystalline. We believe that the control of the substrate temperature is very important to orient the individual grains in these films. Efforts are under way to grow grain-oriented PZT and PLZT films without oxidizing the Si substrate.

D. Growth of PBN:60 Thin Films - Development of single crystal films of tungsten bronze PBN:60 was continued on (100) and (001)-oriented SBN:60 substrates with great success, with films as thick as 5 to 10 μm being obtained. Evaluation of these films indicates that the dielectric constant is close to ceramic samples, implying large longitudinal (r_{51}) electro-optic effects in these films. Since the refractive index difference between PBN:60 (n = 2.41) and SBN:60 (n = 2.24) is large, we are currently engaged in evaluating optical waveguides with these films. Based on these observations, we will make necessary changes in film quality, thickness, and properties.

The growth of tungsten bronze PBN:60 and SBN:75 films has also been successful on (100)-oriented Si substrates as shown in Figure 2. This growth was attempted below 400°C and, for this reason, the films are polycrystalline.

E. Future Planned Work - Since the lattice mismatch between PLZT and PBN:60 compositions is small, we plan to develop a superlattice (multilayer) approach to obtain single crystal films of PLZT and PZT as follows:

1. SBN:60 substrate with 1 to 2 μm PBN:60 film for lattice matching to PLZT or PZT.

2. SBN:60 substrate with 1 to 2 μm PBN:60 film and then alternate PLZT and PBN layers to develop a superlattice structure.

This is the first time these perovskite films will be developed on tungsten bronze substrates for optical waveguides and other applications. Furthermore, the refractive index difference between PBN:60 (n = 2.41) and PLZT (n = 2.71) is large so that one can develop very efficient waveguides in such films.

We will continue to test the utility of PBN:60 films for optical applications and, in parallel, we will explore other applications using these films.

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Ratnakar R. Neurgaonkar
Program Manager

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attachments: Figures 1 and 2

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FIGURE 1

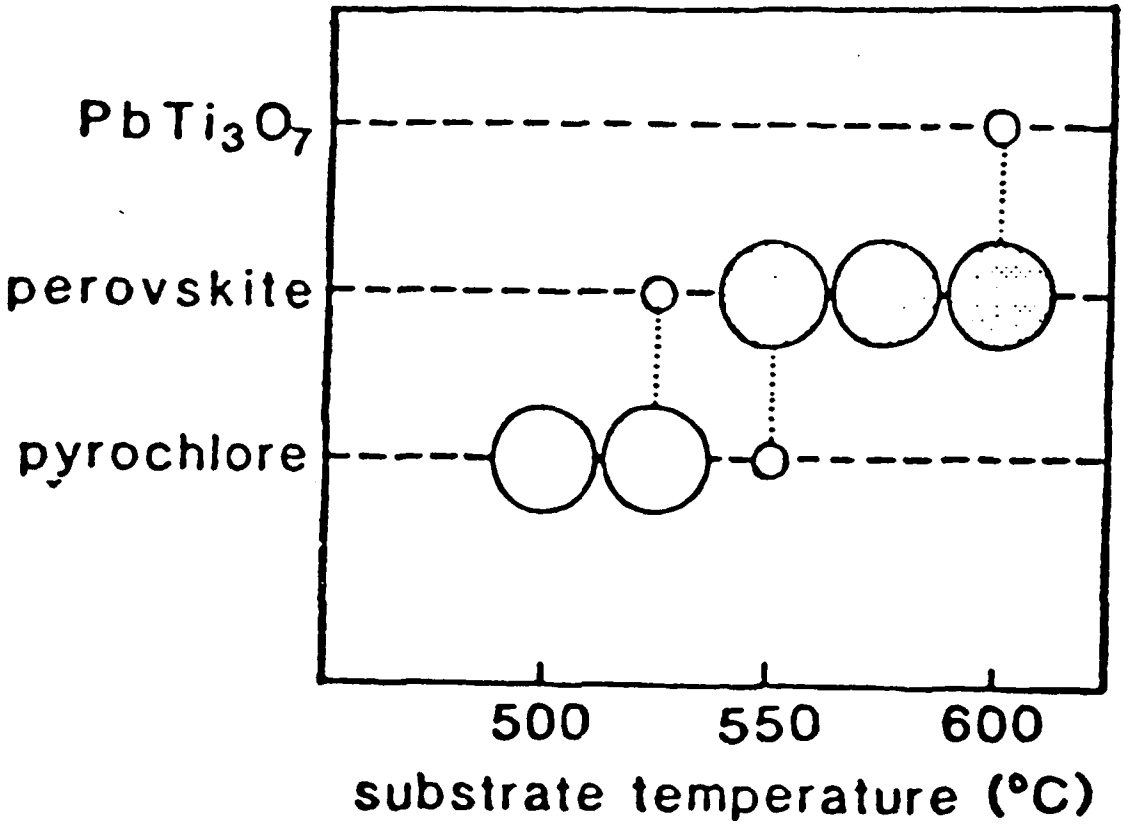

Figure - 1

FIGURE 2

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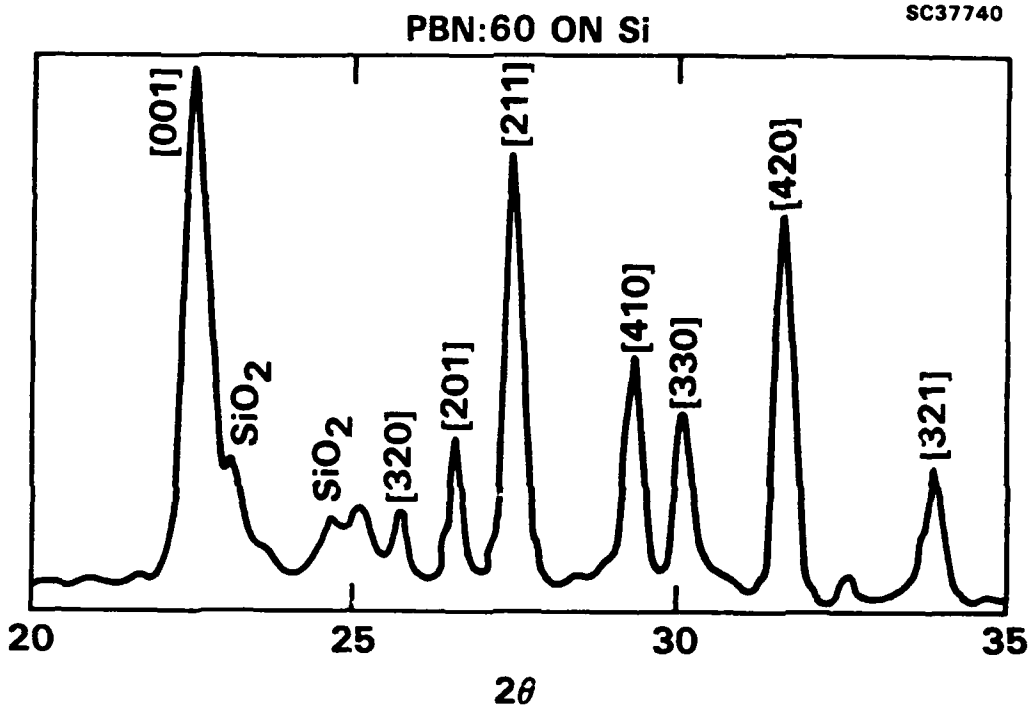

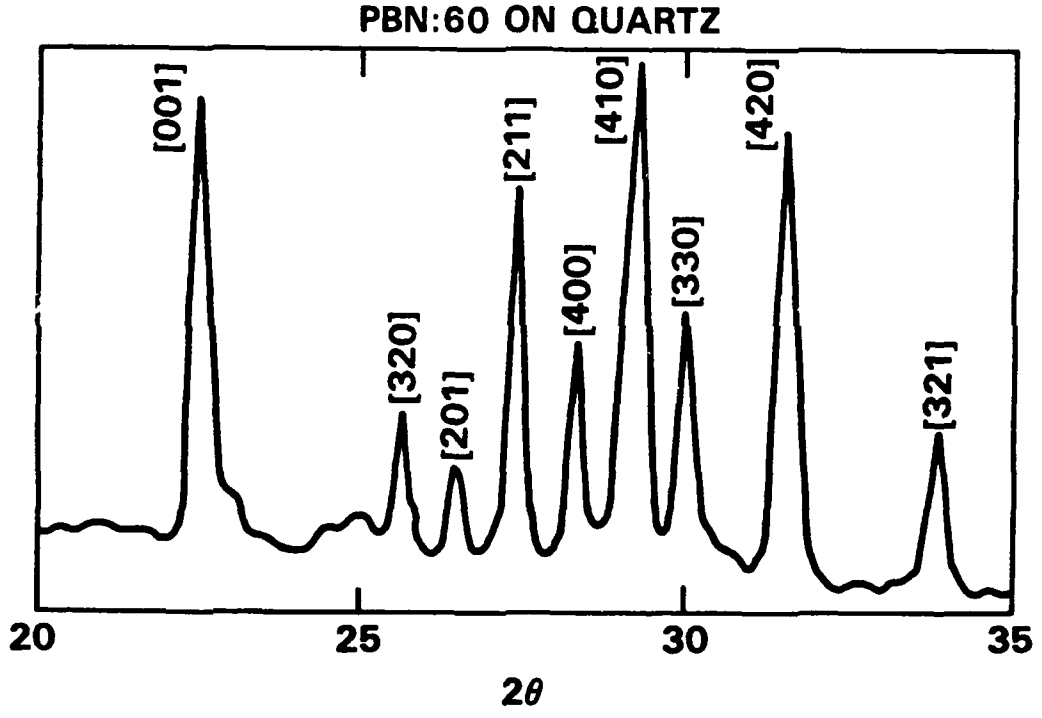

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Figure - 2